ANALYTICA CHIMICA ACTA

Vol. 19 (1958)

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ANALYTICA CHIMICA ACTA

International monthly dealing with every branch of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

Organe Officiel de la Section de Chimie Analytique de l'Union Internationale
de Chimie pure et appliquée

Appointed to publish the official communications
issued by the Section of Analytical Chemistry of the International Union
of Pure and Applied Chemistry

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ELSEVIER PUBLISHING COMPANY
AMSTERDAM LONDON NEW YORK PRINCETON

***Anal. Chim. Acta*, Vol. 19 (1958)**

Printed in The Netherlands by
NEDERLANDSE BOEKDRUK INRICHTING N.V., 'S-HERTOGENBOSCH

REVUE DE LIVRE

Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique, publiées sous la direction de J. A. Gautier, 6è Série, Masson et Cie., Paris, 1958, un volume broché de 172 pages et 60 figures, 2600 francs français.

Le sixième volume de cette collection dont j'ai déjà dit beaucoup de bien et souligné l'originalité et l'utilité comporte six conférences faites en 1957 à la Faculté de Pharmacie de Paris par MM.

P. Devillers – Analyse des produits sucrés industriels et commerciaux: échangeurs d'ions et chromatographie,

Cl. Duval – Applications analytiques de la thermogravimétrie,

J. A. Gautier – Chimie analytique et contrôle des médicaments,

H. Renault – Le dosage de radioéléments en biologie et en radiotoxicologie,

J. P. Wolff – Méthodes physico-chimiques d'analyse des corps gras, et se termine par un index récapitulatif des sujets traités dans les six premières séries de la collection.

Chaque article, accompagné de figures claires est suivi d'une abondante bibliographie et fait une mise au point moderne, scientifique qui permet à chacun de s'évader de sa propre spécialité. Ainsi pour s'en tenir à l'exposé de J. P. Wolff sur l'analyse des corps gras que l'on n'entrevoit habituellement que par la détermination d'un certain nombre d'indices traditionnels, nous trouvons ici les possibilités dans ce domaine de la chromatographie d'absorption et de partage, en phase vapeur, à contre-courant, la spectrophotométrie ultraviolette, dans le visible et dans l'infrarouge, la polarographie, le dosage potentiométrique, etc.

Clément Duval (Paris)

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THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

V. FURTHER APPLICATIONS OF THE NITROAMINO-NAPHTHALENE MONOSULPHONIC ACIDS TO THE FLUORIMETRIC DETECTION OF STANNOUS TIN

by

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INTRODUCTION

The use of 6-nitro-2-aminonaphthalene-8-sulphonic acid[1,2] for the detection and determination of stannous tin has already been described. The application of 8-nitro-2-aminonaphthalene-6-sulphonic acid and two isomeric compounds prepared by the mononitration of 2-aminonaphthalene-5-sulphonic acid to the detection of tin, has also been reported[3]. In a further communication[4], the use of the nitronaphthylamines in the fluorimetric detection of stannous tin has been observed, although, with these compounds, the presence of strong hydrochloric acid in the reagent solution is necessary for maximum sensitivity of test.

In order to study the influence of the sulphonic acid group upon the sensitivity of test, three further nitroamino-naphthalene monosulphonic acids have been synthesized and found to be of use as reagents in the detection of stannous tin. The compounds described in this paper are the ammonium salts of 5-nitro-1-aminonaphthalene-2-sulphonic acid, 4-nitro-1-aminonaphthalene-5-sulphonic acid and 4-nitro-1-aminonaphthalene-6-sulphonic acid. Of 47 metal ions tested as previously reported[1,3,4], only stannous tin gave an intense fluorescence when viewed under ultraviolet light, after quenching of any previous fluorescence with 15N NH_4OH.

EXPERIMENTAL

Preparation of reagents

4-nitro-1-aminonaphthalene-5-sulphonic acid. The following modification of LEVINSTEIN's procedure[5] was used. Urea (0.2 g) was added to 150 ml sulphuric acid (spec. grav. 1.84) followed by 1-aminonaphthalene-5-sulphonic acid (6.5 g), and the solution chilled to 0° by the direct addition of dry ice. A mixture of 1.9 ml of HNO_3 (spec. grav. 1.42) and 2.7 ml of H_2SO_4 (spec. grav. 1.84) was added slowly over a period of 1 h at 0°, the solution stirred for a further hour at this temperature then poured onto 150 g crushed ice whereupon 4-nitro-1-aminonaphthalene-5-sulphonic acid separated out in the form of yellow flakes. The precipitate was macerated with 15N NH_4OH, cooled and filtered. The resulting ammonium salt was purified by recrystallisation from 50% aqueous alcohol in orange needles which were moderately soluble in water. Yield 4.1 g

4-nitro-1-aminonaphthalene-6-sulphonic acid. Using CASSELLA's procedure[6], 1-aminonaphthalene-6-sulphonic acid was nitrated with a mixture of nitric and sulphuric acids. The resulting 4-nitro-

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* On study leave at Birkbeck College, University of London.

1-aminonaphthalene-6-sulphonic acid was isolated as the ammonium salt which crystallised from hot water in orange-yellow needles.

5-nitro-1-aminonaphthalene-2-sulphonic acid. The nitration of 1-aminonaphthalene-2-sulphonic acid by a mixture of nitric–sulphuric acids according to CASSELLA's method[7] yielded 5-nitro-1-aminonaphthalene-2-sulphonic acid. The ammonium salt crystallised in deep red plates from hot water.

Technique of spot testing

Spots of aqueous solutions measuring 0.01 ml and containing 0.1 mg of each of the metal ions, were placed on a sheet of No. 1 Whatman chromatographic paper and sprayed separately with 0.1% aqueous solutions of the reagents. The sheets were air-dried and viewed under ultraviolet light, any fluorescence being noted. The sheets were now sprayed with 15*N* NH_4OH, air-dried and again viewed under ultraviolet light, the quenching of any previous fluorescence being noted. All fluorescence tests were carried out using a Crompton electric discharge lamp 47 (125 W, 230/240 V) with approx. 3650 Å U.V. of radiation.

Reagents used for spot tests

No. 1. 0.1% aqueous solution of the ammonium salt of 5-nitro-1-aminonaphthalene-2-sulphonic acid.
No. 2. 0.1% aqueous solution of the ammonium salt of 4-nitro-1-aminonaphthalene-5-sulphonic acid.
No. 3. 0.1% aqueous solution of the ammonium salt of 4-nitro-1-aminonaphthalene-6-sulphonic acid.

TABLE I

RESULTS OBTAINED FROM SPRAYING SPOTS OF METALLIC IONS WITH VARIOUS REAGENTS BEFORE AND AFTER QUENCHING OF FLUORESCENCE WITH 15*N* NH_4OH

Metal ion	*Reagent number*					
	1		*2*		*3*	
	B	*A*	*B*	*A*	*B*	*A*
Fe^{+2}	F (slight)		F (slight)		F (slight)	
Sn^{+2}	F	F	F	F	F	F
Sn^{+4}	F (slight)		F	F (halo)*	F	F (halo)*
Hg^{+}	F ,,		F (slight)		F (slight)	
Hg^{+2}	F ,,		F ,,		F ,,	
As^{+3}	F ,,		F ,,		F ,,	F (halo)*
Sb^{+3}			F ,,		F ,,	
Bi^{+3}	F (slight)		F ,,		F ,,	F (halo)*
Al^{+3}	F ,,					
Cr^{+3}	F ,,					
Mn^{+2}	F ,,					
Cu^{+2}	F ,,					
Co^{+2}	F ,,					
Ni^{+2}	F ,,					
Ce^{+3}	F ,,		F (slight)		F (slight)	
Pt^{+2}	F (halo)*		F (halo)*	F (halo)*	F (halo)*	
Pt^{+4}	F (slight)		F (slight)		F (slight)	
Au^{+3}	F (halo)*		F (halo)*		F (halo)*	
Pd^{+2}			F (slight)		F (slight)	
Tl^{+3}	F (slight)		F (halo)*	F (halo)*	F (halo)*	F (halo)*
W^{+6}	F ,,	F (slight)	F ,,	F ,,	F ,,	F ,,
Be^{+2}	F ,,	F ,,	F ,,			
UO_2^{+2}	F ,,					
VO^{+2}	F ,,		F (slight)	F (halo)*	F (slight)	
ZrO^{+2}	F ,,	F (slight)	F ,,			
Ru^{+3}			F (halo)*		F (halo)*	F (halo)*
Ti^{+3}	F (slight)	F (slight)	F (slight)			
Ti^{+4}	F ,,	F ,,			F (halo)*	F (halo)*

Other ions tested included:
Fe^{+3}, As^{+5}, Zn^{+2}, Sr^{+2}, Ca^{+2}, Ba^{+2}, Mg^{+2}, Pb^{+2}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, Li^{+}, Mo^{+6}, Tl^{+}, V^{+5}, Th^{+4}, Cd^{+2}, Ag^{+}

B = before quenching; A = after quenching; F = fluorescence.
* F (halo) = faint fluorescent ring around a non-fluorescent spot.

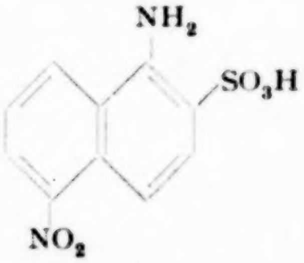
Sensitivity tests for stannous tin were performed using the same procedure as described in previous communications[1,3,4]. Reagent Nos. 2 and 3 were found to be each capable of detecting 10^{-6} g of stannous tin; reagent No. 1, 10^{-5} g and the standard, 6-nitro-2-aminonaphthalene-8-sulphonic acid, 10^{-7} g.

The fluorescent spots of stannous tin were found to be yellowish-green with reagent Nos. 2 and 3; purple-blue with reagent No. 1 and greenish-blue with the standard which also yielded the most intensely fluorescent spots, followed by reagents No. 3, 2 and 1 in order of decreasing intensity of fluorescence.

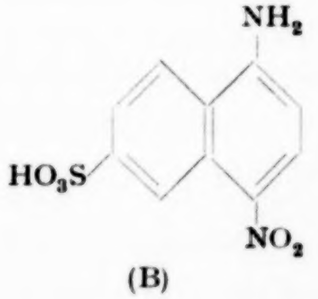
DISCUSSION

It has already been shown that the orientation of the nitro group in the nitro-aminonaphthalene monosulphonic acids does not markedly influence the nature of the stannous tin spot test[3,4]. The test results from reduction of the nitro-aminonaphthalene sulphonic acid by stannous tin to yield a diaminonaphthalene monosulphonic acid which is the compound responsible for the fluorescence.

Enough data is also available at present to adequately assess the effect of the sulphonic acid group in these compounds upon the sensitivity of the tin test. Including the acids used in Parts I, III and V, seven different nitro-aminonaphthalene monosulphonic acids have been examined as reagents and little variation in sensitivity of test has been observed, even with 5-nitro-1-aminonaphthalene-2-sulphonic acid (A). This isomer is particularly important, since the presence of any *"ortho"* effect due to the sulphonic acid group in the 2-position, being adjacent to the amino group, should be evidenced by some appreciable change in sensitivity of the spot test.



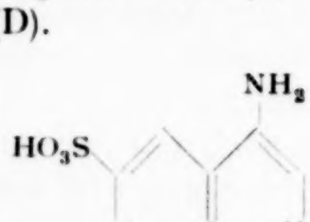
(A)



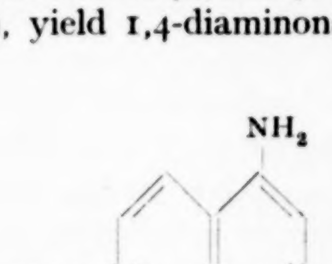
(B)

Furthermore, if the assumption be made that the ease of reduction of the nitro group by tin does not influence the actual species responsible for the fluorescence, then in effect, fourteen nitro-aminonaphthalene-monosulphonic acids have been studied, since any diaminonaphthalene monosulphonic acid can be formed from the reduction of two corresponding nitro-aminonaphthalene monosulphonic acids.

For example, 4-nitro-1-aminonaphthalene-6-sulphonic acid (B) and 4-nitro-1-aminonaphthalene-7-sulphonic acid (C) upon reduction, yield 1,4-diaminonaphthalene-6-sulphonic acid (D).



(C)



(D)

The function of the sulphonic acid group then appears to be essentially one of

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solvolysis of the parent compound towards polar solvents such as water with the subsequent advantage that the spot test may be carried out in aqueous media.

ACKNOWLEDGEMENT

The authors are indebted to Mr. J. T. SNELSON of Geigy (Aust.) Ltd., for samples of 1-aminonaphthalene-5-sulphonic acid and 1-aminonaphthalene-6-sulphonic acid.

One of us, J. R. A. ANDERSON, wishes to thank Professor W. WARDLAW for permission to carry out part of this work at the Department of Chemistry, Birkbeck College, University of London.

SUMMARY

Three new reagents, *viz.* 5-nitro-1-aminonaphthalene-2-sulphonic acid, 4-nitro-1-aminonaphthalene-5-sulphonic acid and 4-nitro-1-aminonaphthalene-6-sulphonic acid, have been found to be of use as fluorimetric spot tests on filter paper for stannous tin. The orientation of the sulphonic acid group does not appear to appreciably affect the sensitivity of the test, approximately one microgram of stannous tin being capable of detection by all isomers.

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Received November 11th, 1957

BEITRÄGE ZUR ANALYTIK EINIGER METHANSULFONSÄUREDERIVATE

I. JODOMETRISCHES VERFAHREN ZUR BESTIMMUNG VON NOVALGIN (NOVAMIDAZOPHEN*) UND MELUBRIN AUCH IN GEGENWART VON ANTIPYRIN (AZOPHEN*) UND PYRAMIDON (AMIDAZOPHEN*)

von

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Beide Aminoantipyrinabkömmlinge: Melubrin und Novalgin (Methylmelubrin) verdanken ihre leichte Wasserlöslichkeit dem an der Aminogruppe kondensierten formaldehydschwefligsauren Natrium. Sie unterscheiden sich lediglich durch eine ebenfalls an der Aminogruppe substituierte Methylgruppe.

Wünscht man daher das Novalgin oder Melubrin auch in Gegenwart von Antipyrin und Pyramidon zu bestimmen, so wendet man sein Augenmerk der für beide Verbindungen charakteristischen Methylsulfonsäuregruppe zu. Die Ausarbeitung einer Bestimmungsmethode dieser Gruppe erschien uns umsomehr möglich als aus den Arbeiten von WINDISCH UND BOCKMÜHL[1] bereits bekannt ist, dass die Kondensation von Formaldehydbisulfiten mit reaktionsfähigen Aminoantipyrinen umkehr-

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* Präparate der Pharmacopoea Hungarica Ed. V.

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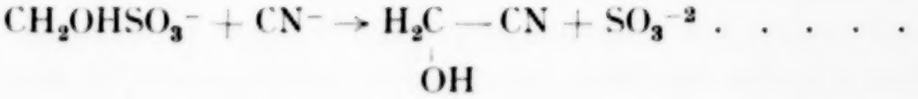
bar ist. Die Verschiebung des auf diese Reaktion charakteristischen Gleichgewichtes in die Richtung des Formaldehyds bzw. schwefliger Säure gelingt besonders in saurer Lösung bei Siedehitze. Auf diese Tatsache gründete Dózsa[2] auf Rat von einem von uns (E.S.) ein Destillationsverfahren, wo der überdampfte Formaldehyd bzw. schweflige Säure zur titrimetrischen Bestimmung gelangte. Der Formaldehyd konnte diesmal nach dem Verfahren von Schulek[3] auch in Gegenwart des reduzierenden Schwefeldioxyds über Bromcyan bequem und genau gemessen werden. Die schweflige Säure wurde dagegen nach Oxydation mit Bromwasser und nach dem Auskochen des Bromüberschusses nach Winkler[4] in Form von $BaSO_4$ gravimetrisch bestimmt, könnte aber ebensogut nach Eindampfen bis zur Trockne azidimetrisch ermittelt werden. Beim letzteren Vorgehen beträgt das Äquivalentgewicht die Hälfte des Molgewichtes. Ein besonderer Nachteil der Dózsa'schen Methode besteht darin, dass der freigelegte Formaldehyd leicht mit dem ebenfalls freigestellten Antipyrinderivat (in Gegenwart von Antipyrin auch mit diesem) kondensiert. Somit kann das Verfahren von Dózsa nur im Mikromasstabe und in Abwesenheit von Antipyrin verwendet werden.

Auf ein anderes Grundprinzip haben Schulek und Menyhárth[5] ihr Verfahren aufgebaut. Das Novalgin wird in diesem Verfahren mittels Permanganat zu einem Oxypyramidonderivat oxydiert und der Permanganat-Überschuss jodometrisch zurückgemessen. Dieses Verfahren wurde auch von der Pharmacopoea Hungarica Ed. V.[5] zur Gehaltsbestimmung von Novamidazophen (Novalgin) aufgenommen. Etwa mit Pyramidon und Aminoantipyrinderivaten verunreinigte, oder zersetzte Präparate weisen dabei oft einen irreführenden höheren Novamidazophengehalt auf. Mit diesem Verfahren können nur frisch bereitete Lösungen (keinesfalls aber labile Fabrikschargen!) analysiert werden.

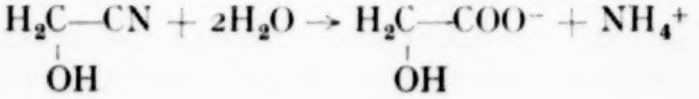
Nach Wirth[6] kann das Novalgin mit Essigsäure leicht angesäuert mit 0.1*N* Jodlösung titriert werden. Nach seiner Meinung erfolgt eine Jodaddition (am 3. und 4. C-Atom) bei dieser Titration. Nach eigenen Versuchen entsteht bei diesem Verfahren Sulfat, was den Wirth's Angaben widerspricht.

Zusammenfassend kann festgestellt werden, dass die beschriebenen Verfahren in Gegenwart von Pyramidon und Antipyrin versagen.

Es ist bereits bekannt, dass die Oxymethansulfonsäuren (Aldehydbisulfite) mit Alkalicyaniden leicht in Reaktion eingehen, wobei Sulfite und Säurenitrile (im Falle von Formaldehydbisulfit Glykolsäurenitril) entstehen.
Die Säurenitrile hydrolysieren sich aber bald in Oxysäuren bzw. Ammoniak. Die Reaktionen können mit folgenden Gleichungen veranschaulicht werden:



$$CH_2OHSO_3^- + CN^- \rightarrow \underset{\displaystyle OH}{H_2C}—CN + SO_3^{-2} \quad . \; . \; . \; . \; . \quad (1)$$



$$\underset{\displaystyle OH}{H_2C}—CN + 2H_2O \rightarrow \underset{\displaystyle OH}{H_2C}—COO^- + NH_4^+ \quad . \; . \; . \; . \; . \quad (2)$$

Auf Grund dieser Tatsache hat einer von uns (L.M.) ein jodometrisches Verfahren zur Bestimmung der Formaldehydbisulfite neben Formaldehyd und Rongalit ausgearbeitet[7], da die schweflige Säure sich in schwach saurer Lösung auch in Gegenwart von Glykolsäure und Ammonsalze mit Jodlösung genau messen lässt.

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Wie unsere diesbezüglichen Versuche zeigten, lassen sich die Kondensationsabkömmlinge des Formaldehydbisulfits in leicht alkalischer Lösung durch Kaliumcyanid auch spalten. So das Novalgin und auch das Melubrin. Im Falle von Melubrin erfolgt die vollständige Spaltung durch KCN allerdings nur beim mässigen Erwärmen der alkalischen Reaktionsflüssigkeit. Das eine Spaltungsstück, das Sulfit kann in leicht schwefelsaurer Lösung auch in Gegenwart der übrigen Spaltungsstücke (Aminoantipyrin, Methylaminoantipyrin, Glykolsäure, Ammonsalz), sowie in Gegenwart von Antipyrin und Pyramidon jodometrisch mit ausreichender Genauigkeit gemessen werden, da die Reaktion zwischen Jod und schwefliger Säure mit bedeutend grösserer Geschwindigkeit als zwischen Jod und Antipyrin, Pyramidon usw. abläuft. Ein Hindernis zeigte doch die Anwesenheit des Cyanidüberschusses, da das Cyanidion bekanntlich auch in mässig saurer Lösung mit Jod im Sinne der Gleichung:

$$CN^- + J_2 \rightleftarrows CNJ + J^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

reagiert[8], wodurch kleinere Unstimmigkeiten im Jodverbrauch besonders beim Arbeiten in 0.01 N Masstab entstehen können. Wird in der Titrierflüssigkeit vor dem Titrieren Kaliumjodid gelöst, so wird die Fehlermöglichkeit durch Verschiebung nach links des in der Gleichung (3) veranschaulichten Gleichgewichtes zurückgedrängt, bzw. behoben.

Es wurde bereits erwähnt, dass das Novalgin im WIRTH'schen Verfahren in essigsaurer Lösung mit J_2-Lösung reagiert. Diese Reaktion — angeblich eine Jodaddition — ist aber keinesfalls eindeutig. Der Jodverbrauch einer mit Schwefelsäure auf pH 1–2 angesäuerter Novalginlösung ist nämlich nach eigenen Versuchen bedeutend kleiner. Bemerkenswerterweise wird das mit Novalgin eng verwandte Melubrin nach EVERS[9] in einer mit Natriumazetat gepufferter Lösung mit vier Äquivalenten Jod oxydiert, wobei angeblich über 4-Formaminoantipyrin 4-Aminoantipyrin entsteht.

Um ein richtiges Urteil zu fassen haben wir mit einem ungarischen Novamidazophen-Präparat (Novalgin) vergleichende Versuche mit dem weiter unten genau beschriebenen „Cyanidverfahren" und dem WIRTH'schen Verfahren[6] ausgeführt. Das Präparat erwies sich nach dem Cyanidverfahren als 98.3 ± 0.1%-ig, nach der WIRTH'schen Methode in leicht essigsaurer Lösung als 111.6 ± 2%-ig. Als wir aber die Lösung anstatt Essigsäure mit wenig Schwefelsäure ansäuerten, so fielen die Resultate bedeutend niedriger: auf 86.4 ± 2% ab. Es ist bemerkenswert, dass bei den schwefelsauren Versuchen der Jodverbrauch umso mehr sich verminderte, je später die Lösung nach der Ansäuerung titriert wurde. Solche Verminderung des Jodverbrauches, bzw. Schwankungen in den Ergebnissen war bei der „Cyanidmethode" auch nach 8 Stunden Wartezeit nicht zu beobachten.

Die Ursache der oben angeführten interessanten Versuchsergebnisse ist unserer Meinung in der hydrolytischen Spaltung des Novalgins in der verdünnten Lösung (etwa 0.05 M) zu suchen. Das bei dieser Hydrolyse entstandene Formaldehydbisulfit wird in mit Schwefelsäure mässig angesäuerten Jodlösung nicht angegriffen. Damit können die niedrigeren Versuchsergebnisse erklärt werden. Die streng nach der WIRTH'schen Vorschrift ausgeführten Versuche in mit Essigsäure angesäuerter, also einigermassen gepufferter Lösung weisen einen bedeutend grösseren Prozentgehalt an Novalgin (111.6 ± 2%) auf, da in diesem Verfahren mit einer teilweisen Oxydation im Sinne des EVERS'schen[9] Mechanismus zu rechnen ist.

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Bei der Anwendung des von uns in Vorschlag gebrachten „Cyanidverfahren" sind die beschriebenen Fehlermöglichkeiten allerdings auch in Gegenwart von Antipyrin und Pyramidon nicht zu befürchten.

BESCHREIBUNG DES VERFAHRENS

Reagenzien

0.1*N* Jodlösung
10%-ige Natronlauge
50%-ige Schwefelsäure
1%-ige, mit 0.1% Salicylsäure abgebaute bzw. konservierte Stärkelösung
0.2%-ige alkoholische Methylrotlösung
Kaliumcyanid fest, analysenrein
Kaliumjodid fest, analysenrein
Pentan, analysenrein.

Die mit analytischer Genauigkeit eingewogene 1.7–1.9 g Untersuchungssubstanz (Novalgin bzw. Melubrin) wird in einem Messkolben von 100 ml Inhalt in dest. Wasser gelöst und bis zur Marke ergänzt. 10.00 ml der Stammlösung wird nun in einem, mit Glasstöpsel verschliessbaren Erlenmeyer-Kolben von 100 ml Inhalt, mit 40 ml frisch ausgekochten und schnell abgekühlten Wasser versetzt, mit wenig (1–2 ml) Pentan bedeckt um die störende Einwirkung des Luftsauerstoffes zu verhüten. Nun wird die Lösung mit 5 ml 10%-iger Natronlauge und mit 0.2–0.3 g festem Kaliumcyanid versetzt. Im Falle von Melubrin wird die auf 50 ml ergänzte Lösung (ohne Pentanschicht!) etwa bis zum Sieden erwärmt, mit 5 ml 10%-iger Natronlauge und mit 0.2–0.3 g festem Kaliumcyanid versetzt, dann nach 2–3 Minuten auf Zimmertemperatur abgekühlt, endlich mit Pentanschicht versehen. Nach 2–3 Minuten Wartezeit — diese Zeit genügt zur vollständigen Abspaltung der Sulfite — neutralisiert man zuerst die Lösung unter Umschwenken aus einer auf 0.01 ml eingeteilter Pipette mit 50%-iger Schwefelsäure in Gegenwart von einem Tropfen Methylrotlösung um dann dieselbe mit weiteren 0.5 ml Schwefelsäure anzusäuern. Nach Hinzufügen von 0.2 g Kaliumjodid wird die Lösung in Gegenwart von Stärkelösung mit 0.1*N* Jodlösung titriert. In der Nähe des Endpunktes wird die Titrierflüssigkeit tropfenweise zugegeben. Im Endpunkt zeigt die Lösung eine 40–60 Sekunden dauernde violette Farbe.

Das Äquivalentgewicht beträgt die Hälfte des Molgewichtes (175.68 Novalgin bzw. 168.67 Melubrin).

Das Verfahren liefert auch in Gegenwart von Antipyrin und Pyramidon befriedigende Resultate. Die Analysenergebnisse sind in den Tabellen I–V zusammengestellt.

TABELLE I

NOVALGIN (NOVAMIDAZOPHEN)-BESTIMMUNGEN, CYANIDVERFAHREN

Benennung u. Herkunft der Untersuchungssubstanz	*Einwaage Novalgin bzw. Novamidazophen*		*Verbraucht 0.1N J_2-Lösung ml*		*Gefunden Novalgin (Novamidazophen)*
	g/200 ml	*ml*	*einzeln*	*M-Wert*	%
Novamidazophen (Novalgin) „Magyar Pharma, Budapest" (umkristallisiert!)	3.3220	10.00	9.47 9.48 9.47 9.46	9.47	100.1
Novalgin (Novamidazophen) „I. G. Farbenindustrie"	3.5165	10.00	9.90 9.88 9.90 9.89	9.90	98.9
Novamidazophen (Novalgin) „Chinoin, Budapest"	3.5065	10.00	9.80 9.81 9.81 9.82	9.81	98.3

TABELLE II

NOVALGIN (NOVAMIDAZOPHEN)-BESTIMMUNGEN IN GEGENWART VON ANTIPYRIN, CYANIDVERFAHREN

Einwaage				*Verbraucht 0.1N J_2-Lösung ml*		*Gefunden Novalgin (Novamidazophen)*
Novamidazophen „Chinoin" g/200 ml	*Antipyrin g/200 ml*	*Novamidazophen Lösung ml*	*Antipyrin-Lösung ml*	*einzeln*	*M-Wert*	%
3.5065	4.9290	10.00	—	9.80 9.81 9.81	9.81	98.3
		10.00	5.00	9.80 9.82 9.81	9.81	98.3
		10.00	10.00	9.81 9.80 9.80	9.80	98.2
		10.00	20.00	9.81 9.82 9.81	9.81	98.3

TABELLE III

NOVALGIN (NOVAMIDAZOPHEN)-BESTIMMUNGEN IN GEGENWART VON PYRAMIDON, CYANIDVERFAHREN

Einwaage				*Verbraucht 0.1N J_2-Lösung ml*		*Gefunden Novalgin (Novamidazophen)*
Novamidazophen „Magyar Pharma" g/200 ml	*Pyramidon g/200 ml*	*Novamidazophen-Lösung ml*	*Pyramidon-Lösung ml*	*einzeln*	*M-Wert*	%
3.3220	2.3610	10.00	—	9.47 9.48 9.47	9.47	100.1
		10.00	5.00	9.46 9.48 9.47	9.47	100.1
		10.00	10.00	9.48 9.46 9.47	9.47	100,1
		10.00	20.00	9.48 9.47 9.48	9.48	100,2

TABELLE IV

MELUBRIN-BESTIMMUNGEN IN GEGENWART VON ANTIPYRIN UND PYRAMIDON, CYANIDVERFAHREN

Einwaage						*Verbraucht 0.1N J_2-Lösung ml*		*Gefunden Melubrin*
Melubrin g/200 ml	*Antipyrin g/200 ml*	*Pyramidon g/200 ml*	*Melubrin-Lösung ml*	*Antipyrin-Lösung ml*	*Pyramidon-Lösung ml*	*einzeln*	*M-Wert*	%
3.3890	3.5830	3.4064	10.00	—	—	9.94 9.94 9.95	9.94	98.9
			10.00	5.00	5.00	9.95 9.96 9.95	9.95	99.0
			10.00	20.00	20.00	9.95 9.94 9.96	9.95	99.0

TABELLE V

NOVALGIN (NOVAMIDAZOPHEN)-BESTIMMUNGEN IN GEGENWART VON ANTIPYRIN UND PYRAMIDON, CYANIDVERFAHREN

Einwaage						*Verbaucht 0.1N J_2-Lösung ml*		*Gefunden Novalgin (Novamidazophen)*
Novamidazophen „Chinoin" g/200 ml	*Antipyrin g/200 ml*	*Pyramidon g/200 ml*	*Novamidazophen-Lösung ml*	*Antipyrin-Lösung ml*	*Pyramidon-Lösung ml*	*einzeln*	*M-Wert*	*%*
3.5165	3.5061	4.9290	10.00	—	—	9.90 9.88 9.90	9.90	98.9
			10.00	5.00	5.00	9.90 9.89 9.91	9.90	98.9
			10.00	10.00	10.00	9.89 9.89 9.88	9.89	98.8
			10.00	20.00	20.00	9.90 9.90 9.90	9.90	98.9

ZUSAMMENFASSUNG

Verfasser haben ein jodometrisches Verfahren zur Bestimmung von arzneilich verwendeten Methansulfonsäureabkömmlingen (diesmal zur Bestimmung von Novalgin bzw. Melubrin auch in Gegenwart von Antipyrin und Pyramidon) in Vorschlag gebracht. Das Verfahren wurde auf die Tatsache aufgebaut, dass einige Methansulfonsäureabkömmlinge (Novalgin, Melubrin) sich in mässig alkalischer Lösung durch Kaliumcyanid in Sulfite, Glykolsäure usw. spalten lassen. Die Sulfite können nun in mässig schwefelsaurer Lösung auch in Gegenwart von den Spaltprodukten sowie von überschüssigem HCN, aber auch in Gegenwart von Antipyrin und Pyramidon unter den angegebenen Verhältnissen mit Jodlösung direkt titriert werden.

SUMMARY

An iodometric method is presented for the determination of methanesulphonic acid derivatives that are used in medicine. Here the method was applied to the determination of novalgin and melubrin, alone or in the presence of antipyrine and pyramidone. The method is based on the fact that in moderately alkaline solution some methanesulphonic acid derivatives (novalgin, melubrin) can be split into sulphite and glycolic acid, etc., by potassium cyanide. The sulphite can then be directly titrated with iodine solution, this titration being carried out in sulphuric acid solution of moderate concentration. Under the conditions indicated the titration can be performed in the presence of the degradation products and of excess HCN, as well as in the presence of antipyrine and pyramidone.

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Eingegangen den 17. Oktober 1957

VOLUMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS

XII. OXIDATION WITH SODIUM HYPOCHLORITE IODINE MONOCHLORIDE METHOD

by

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Because sodium hypochlorite is a highly reactive substance, it is believed to be too unstable to be used as a standard titrimetric reagent. JELLINEK AND KRESTEFF[1] used sodium hypochlorite for the determination of arsenious chloride, stannous chloride and antimonous chloride, and also estimated arsenic and antimony in alloys. GOLDSTONE AND JACOBS[2] recommended the use of alkaline sodium hypochlorite solution as a titrimetric reagent for microanalytical work. They showed that the chlorometric determinations can be carried out at room temperature with accuracy and sharpness of end point, using methyl orange as an indicator. KITCHENER *et al.*[3] have investigated the oxidizing properties of alkaline sodium hypochlorite. They found that the reagent was stable to boiling and that it quantitatively oxidizes sulphide to sulphate:

$$4\ ClO^- + S^{-2} \rightarrow 4\ Cl^- + SO_4^{-2}$$

ERDEY AND BUZÁS[4] used $0.1\,N$ sodium hypochlorite solution in redox titrations for the estimation of arsenious oxide, hydrazine sulphate, tartar emetic, sodium thiosulphate, employing luminol as an indicator. As no suitable indicator could be found for the volumetric estimation of tripositive antimony with alkaline sodium hypochlorite, KHÁTUN AND KHUNDKAR[5] developed a potentiometric method for the determination of the antimony at temperatures above 75°.

In this investigation, alkaline sodium hypochlorite was used as an oxidant for the volumetric determination at room temperature of arsenious oxide, hydrazine sulphate, ferrous ammonium sulphate, stannous chloride, sodium sulphite, potassium iodide, mercurous chloride, thallous chloride and tartar emetic in the presence of iodine monochloride as a catalyst and preoxidizer.

EXPERIMENTAL

Alkaline sodium hypochlorite $0.0971\,N$ was prepared by passing chlorine into sodium hydroxide $0.4\,N$, boiling the solution and finally standardizing it by an iodometric method according to KITCHENER *et al.*[3].

A known weight of each substance was placed in a conical flask and about 10 ml of water, 20 ml of concentrated hydrochloric acid, 5 ml of $0.2\,M$ iodine monochloride, and 5 ml of chloroform were added. The mixture was cooled to room temperature and titrated with $0.0971\,N$ sodium hypochlorite solution. The reagent was added from a burette until the solution, which was coloured with iodine, became pale yellow and the chloroform layer acquired a purple colour due to the iodine. The conical flask was stoppered and vigorously shaken during the titration.

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Addition of small volumes of the hypochlorite solution was continued, shaking vigorously after each addition, until the chloroform layer was faintly violet. The hypochlorite was then added dropwise, again shaking the solution after the addition of each drop, until the chloroform layer became pale yellow. The end-point was very sharp. In these titrations, normality of the solution with respect to hydrochloric acid was kept between $5N$ and $7N$. Several titrations were performed in each case. From the volume of the sodium hypochlorite used, corresponding to the end-point in each titration, the amount of each substance was calculated.

Some typical results given in Table I show that the substances used in this study can be determined by the volumetric method, using sodium hypochlorite as an oxidizing agent.

TABLE I

TITRATION OF VARIOUS REDUCING AGENTS WITH $0.0971N$ SODIUM HYPOCHLORITE

Reducing agent titrated	*Weight of reducing agent* *Taken* *g*	 *Found* *g*
As_2O_3	0.0245	0.0244
	0.1129	0.1127
$NH_2{\cdot}NH_2{\cdot}H_2SO_4$	0.0092	0.0092
	0.0676	0.0675
$FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$	0.1152	0.1153
	0.6529	0.6527
$SnCl_2{\cdot}2H_2O$	0.0611	0.0610
	0.1631	0.1631
Na_2SO_3	0.0252	0.0252
	0.1004	0.1004
KI	0.0323	0.0322
	0.1294	0.1295
Hg_2Cl_2	0.1186	0.1186
	0.3105	0.3105
TlCl	0.0652	0.0651
	0.2004	0.2004
$\begin{matrix}CH(OH)COOK\\ CH(OH)COO(SbO)\end{matrix}\cdot\frac{1}{2}H_2O$	0.0835	0.0834
	0.2505	0.2503

SUMMARY

Alkaline sodium hypochlorite was used as an oxidant to determine arsenious oxide, hydrazine sulphate, ferrous ammonium sulphate, stannous chloride, sodium sulphite, potassium iodide, mercurous chloride, thallous chloride and tartar emetic, by a volumetric method, using iodine monochloride as catalyst and preoxidizer. During these titrations, the normality of the solution with respect to hydrochloric acid was kept between $5N$ and $7N$. Chloroform was used as an indicator. Its pink colour due to the liberation of iodine during the titration turns very pale yellow at the end-point because of the formation of iodine monochloride.

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Received October 21st, 1957

COUNTERCURRENT EXTRACTION SEPARATION OF SOME PLATINUM GROUP METALS

by

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Solvent extraction has not been widely used as a means of resolving mixtures of the platinum group metals. The reviews of IRVING[1] and MCBRYDE[2] indicate that only a few applications have been found for solvent extraction in the analyzing of the platinum group metals. MORRISON AND FREISER'S[3] extensive survey of extraction systems confirms that little has been done on extracting precious metals.

The purpose of this work was to develop some new methods for resolving mixtures of platinum, palladium, rhodium, and iridium. Solvent extraction techniques were selected because they are generally rapid, simple, economical, and selective enough to resolve similar substances.

Since the platinum group metals are usually maintained in solution as their chloro-complexes, it was decided to attempt a separation based on the selective extraction of the chloro-complexes. Distribution coefficients were determined for the partitioning of the chloro-complexes between hydrochloric acid solution and tributyl phosphate. The results indicated that mixtures of rhodium and iridium, rhodium and platinum, and platinum and palladium could be resolved by countercurrent distribution.

EXPERIMENTAL

Apparatus

A Beckman Model DU spectrophotometer with matching silica cells was used for the analysis of the platinum, palladium, rhodium and iridium solutions.

The countercurrent distribution apparatus was an extraction machine based on the design of CRAIG AND POST[4].

Reagents

A standard platinum solution was prepared by dissolving a known weight of platinum thermocouple wire in aqua-regia. The solution was repeatedly evaporated to dryness and taken up in concentrated hydrochloric acid to remove all nitrate derivatives. Finally, the residue was taken up in 100 ml of concentrated hydrochloric acid and diluted to one liter with distilled water.

Palladium metal was dissolved in perchloric acid. The solution was fumed to dryness and the residue dissolved in 100 ml of concentrated hydrochloric acid before being diluted to one liter with distilled water. The solution was standardized by precipitation analysis using dimethylglyoxime reagent.

The rhodium stock solution was prepared by dissolving rhodium(III) chloride from A. D. Mackay, Inc., in 100 ml of concentrated hydrochloric acid. The solution was then diluted to one liter and standardized by spectrophotometric analysis using the method of AYRES AND YOUNG[5]. Spectrophotometric standards were verified by the method of GILCHRIST[6].

The iridium stock solution was prepared by dissolving iridium(IV) chloride from A. D. Mackay, Inc., in 100 ml of concentrated hydrochloric acid. The solution was then diluted to one liter and standardized by spectrophotometric analysis using the method of AYRES AND QUICK[7]. Spectrophotometric standards were verified by the method of GILCHRIST[6].

Analytical procedures

Samples to be analyzed for platinum were treated with aqua-regia and evaporated to a moist residue. Concentrated hydrochloric acid was added and the sample again evaporated to a moist residue. The sample was then taken up in approximately 10% hydrochloric acid and analyzed by the method of AYRES AND MEYER[8].

The initial step in the analysis of a sample for palladium was to fume the sample down with a mixture of 95 parts perchloric acid and 5 parts nitric acid. The sample was then dissolved in concentrated hydrochloric acid and taken down to a moist residue. The sample was then dissolved in 3% hydrochloric acid and analyzed by the method of AYRES AND TUFFLY[9].

The rhodium sample was evaporated to a moist residue after addition of aqua-regia. The moist residue was dissolved in concentrated hydrochloric acid and evaporated to dryness. The sample was dissolved in 3% hydrochloric acid and analyzed by the method of AYRES AND YOUNG[5].

Iridium samples were evaporated to a moist residue in aqua-regia. The residue was dissolved in 10% hydrochloric acid and analyzed for iridium by the method of AYRES AND QUICK[7].

Measurement of distribution coefficients

The procedures followed for measuring the distribution coefficients of the chloro-complexes of platinum, palladium, rhodium and iridium were identical, hence the procedure described below applies in all four cases.

Six 5.00-ml aliquots of the stock sample solution were taken to dryness on the steam bath. The samples were then dissolved in appropriate amounts of concentrated hydrochloric acid. Upon dilution to 15 ml, the molar concentration of the hydrochloric acid in the six samples was 1, 2, 3, 5, 7 and 9 respectively. The systems were then saturated with sodium chloride. Ten ml of tributyl phosphate was added to the system and the two phases were equilibrated by repeated inversion of the tubes.

The raffinate (aqueous phase) was filtered through Whatman No. 1 filter paper. This eliminated the contamination of the raffinate by the extractant, as the extractant would not pass through the wet filter paper. The raffinate was then analyzed for the appropriate metal.

A graphical picture of the variation of the distribution coefficient with molarity of hydrochloric acid may be seen in Fig. 1. The distribution coefficient is defined as:

$$K_d = \frac{\text{mg metal/ml of extractant}}{\text{mg metal/ml of raffinate}}$$

Separation of platinum and palladium

The sample containing a mixture of platinum and palladium was evaporated to dryness on a steam bath. The residue was dissolved in $3M$ hydrochloric acid saturated with sodium chloride and tributyl phosphate. The sample solution was heated for ten minutes on a steam bath, cooled and transferred to tube 0 in the countercurrent extraction apparatus. The other tubes were filled with the raffinate, $3M$ hydrochloric acid saturated with sodium chloride and tributyl phosphate. Then 18 ml of tributyl phosphate were added to tube 0. The system was equilibrated by inverting the tube twenty times and then allowing the phases to separate. The extractant from tube 0 was then transferred to tube 1 and fresh extractant added to tube 0. This procedure was repeated until the initial aliquot of extractant was transferred to tube 16. The precious metals were then stripped from each extractant phase by equilibration with 15 ml of a 25% nitric acid solution saturated with sodium nitrate. The raffinate fraction from each tube was combined with the strippings from their respective extractant phases and the metals were analyzed for by the procedures given above.

The separation was run four times and the recovery data are shown in Table I. The average recovery of platinum was 12.98 mg of the 13.38 mg taken. Palladium was recovered to the extent of the 10.00 mg taken.

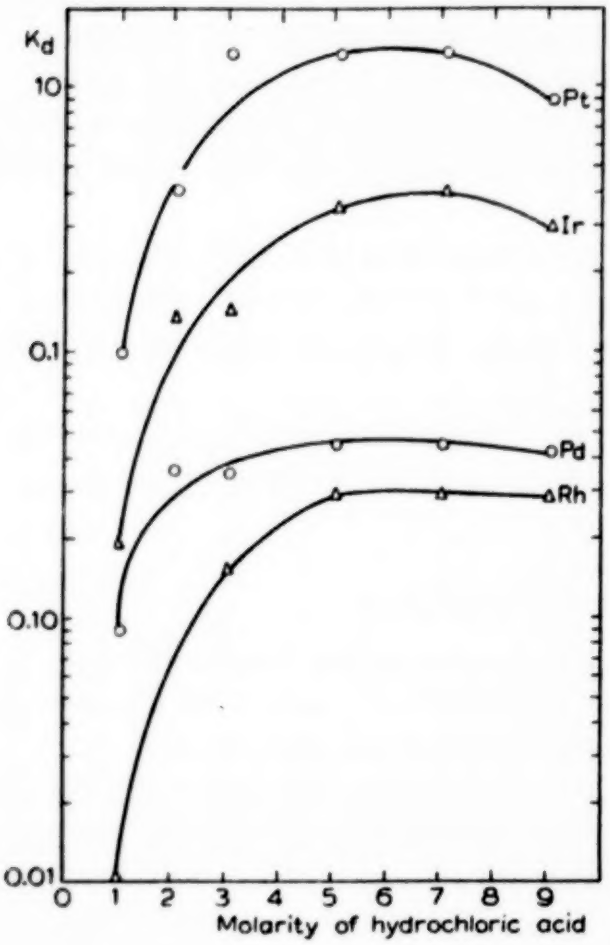

Fig. 1. The variation of the distribution coefficient.

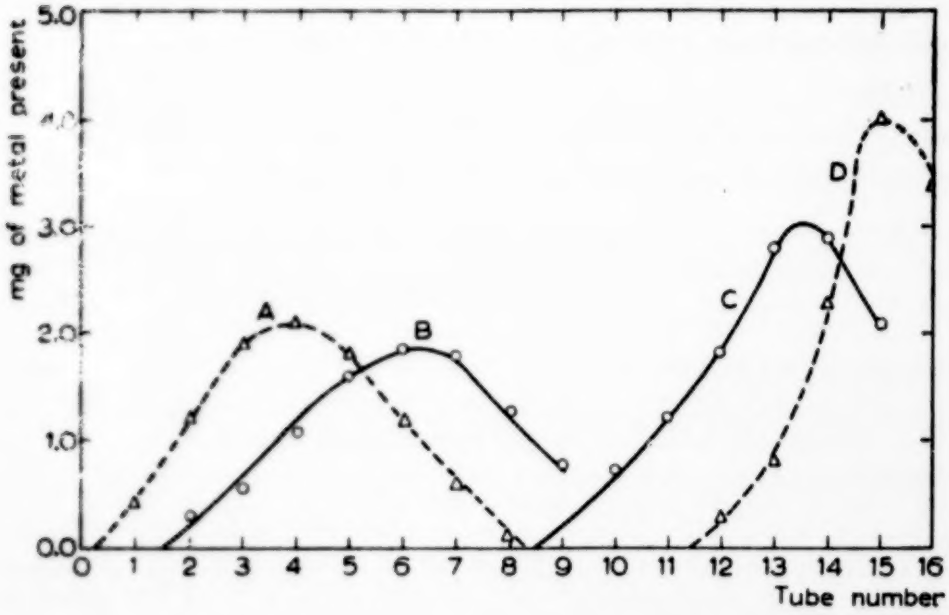

Fig. 2. Distribution curves for the separation of platinum and palladium. A – Theoretical palladium curve. B – Experimental palladium curve. C – Experimental platinum curve. D – Theoretical platinum curve.

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TABLE I

DATA FOR THE SEPARATION OF PLATINUM AND PALLADIUM

System: Hydrochloric acid–sodium chloride–tributyl phosphate. Quantities taken: 13.38 mg o platinum and 10.00 mg of palladium.

	Run No. 1		*Run No. 2*		*Run No. 3*		*Run No. 4*	
Tube No.	*mg Pd*	*mg Pt*	*mg Pd*	*mg Pt*	*mg Pd*	*mg Pt*	*mg Pd*	*mg Pt*
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	tr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.36	0.00	tr	0.00	0.36	0.00	0.44	0.00
3	0.82	0.00	0.36	0.00	0.58	0.00	0.48	0.00
4	1.46	0.00	0.90	0.00	1.02	0.00	1.00	0.00
5	1.82	0.00	1.52	0.00	1.60	0.00	1.48	0.00
6	1.78	0.00	1.90	0.00	1.98	0.00	1.82	0.00
7	1.56	0.00	2.00	0.00	1.90	0.00	1.76	0.00
8	0.90	0.00	1.58	0.00	1.40	0.00	1.24	0.00
9	0.46	0.00	1.08	0.00	0.92	0.00	0.70	0.00
10	0.00	0.40	tr	0.90	0.00	0.70	tr	0.96
11	0.00	0.84	0.00	1.06	0.00	1.56	0.00	1.46
12	0.00	1.56	0.00	1.72	0.00	2.10	0.00	1.98
13	0.00	2.30	0.00	2.88	0.00	3.16	0.00	2.90
14	0.00	3.10	0.00	2.92	0.00	2.70	0.00	2.90
15	0.00	2.76	0.00	2.42	0.00	1.70	0.00	1.60
16	0.00	2.02	0.00	1.22	0.00	1.00	0.00	1.08

Average recovery of platinum = 12.98 mg.
Average recovery of palladium = 9.30 mg.

CRAIG AND CRAIG[10] have shown that the fraction of substance, $T_{n,R}$, present in the Rth tube after n transfers is the Rth term of the binomial theorem. Namely,

$$T_{n,R} = \frac{n!}{R!\,(n-R)!}\left(\frac{1}{K_d+1}\right)^n K_d^R$$

This formula was used to calculate the theoretical distribution of platinum and palladium in the seventeen stages of the countercurrent extraction apparatus. A plot of the amount of metal calculated and found *versus* the tube number is shown in Fig. 2.

Separation of platinum and rhodium

Mixtures of platinum and rhodium were evaporated to dryness on a steam bath and dissolved in $3M$ hydrochloric acid that had been previously saturated with sodium chloride and tributyl phosphate. The sample was heated ten minutes on a steam bath, cooled and transferred to the first tube in the countercurrent extractor. The other tubes in the extractor were filled with the raffinate system, $3M$ hydrochloric acid saturated with sodium chloride and tributyl phosphate. The final volume of the raffinate systems in the tubes was approximately 40 ml. Then 24 ml of tributyl phosphate, saturated with $3M$ hydrochloric acid, was added to tube 0. The system was equilibrated by inverting the tube twenty times before letting the phases separate. Then the extractant phase was transferred to tube 1 and fresh extractant added to tube 0. This procedure was repeated until the initial extractant had been transferred to tube 5, at which point the resolution had been affected. The extractant phase was stripped of the precious metal by equilibration with a 25% solution of nitric acid saturated with sodium nitrate. The stripping solution was combined with the respective raffinate phase and the metals were analyzed for by the procedures given above.

The separation was run four times and the recovery data are shown in Table II. Fig. 3 shows a comparison of the theoretical and actual distribution of platinum and rhodium in the various stages.

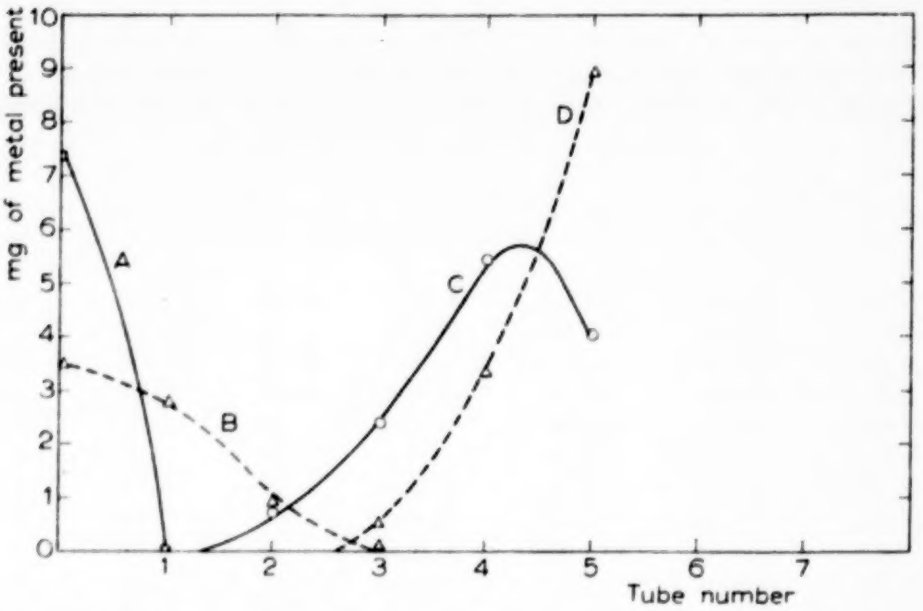

Fig. 3. Distribution curves for the separation of rhodium and platinum. A – Experimental rhodium curve. B – Theoretical rhodium curve. C – Experimental platinum curve. D – Theoretical platinum curve.

TABLE II

DATA FOR THE SEPARATION OF PLATINUM AND RHODIUM

System: Hydrochloric acid–sodium chloride–tributyl phosphate. Quantities taken: 13.38 mg of platinum and 7.40 mg of rhodium

	Run No. 1		*Run No. 2*		*Run No. 3*		*Run No. 4*	
Tube No.	*mg Rh*	*mg Pt*	*mg Rh*	*mg Pt*	*mg Rh*	*mg Pt*	*mg Rh*	*mg Pt*
0	7.24	0.00	7.56	0.00	7.40	0.00	7.30	0.00
1	0.20	0.00	tr	0.00	tr	0.00	tr	0.00
2	0.00	0.00	0.00	1.44	0.00	0.70	0.00	0.90
3	0.00	2.90	0.00	2.04	0.00	2.50	0.00	2.20
4	0.00	5.26	0.00	5.42	0.00	5.62	0.00	5.40
5	0.00	4.10	0.00	4.02	0.00	3.98	0.00	4.80

Average recovery of rhodium = 7.42 mg.
Average recovery of platinum = 12.64 mg.

DISCUSSION

A point for discussion, in the extraction of platinum, palladium, rhodium and iridium as the chlorides, is the type of species extracted. The theory pertaining to the extraction of inorganic solutes postulates the formation of an uncharged complex which may form in two ways, by coordination or ion association. Using iridium(IV) as an example, several possible extraction mechanisms might be outlined.

(a) The formation of an undissociated acid which extracts

$$Ir^{+4} + 6\,Cl^- \rightleftharpoons [IrCl_6]^{-2}$$

Raffinate | Extractant

$$[IrCl_6]^{-2} + 2\,H^+ \rightleftharpoons H_2[IrCl_6] \rightleftharpoons H_2[IrCl_6]$$

(b) The formation of a neutral complex

Raffinate | Extractant

$$Ir^{+4} + 4\,Cl^- \rightleftharpoons IrCl_4 \rightleftharpoons IrCl_4$$

Considering the two situations, (a) appears to be the more probable for two reasons. First the variation of the distribution coefficient with hydrochloric acid concentration reflects more of a dependance than (b) indicates. Also the stability of the $[IrCl_6]^{-2}$ complex is such as to almost preclude the formation of $IrCl_4$. Similar situations exist in the cases of the three other metals studied.

The separation of rhodium and iridium in the chloride system was first attempted on the countercurrent extractor. Only a partial resolution was obtained. The iridium remaining in the rhodium fraction could not be extracted. After hydrogen peroxide was added to the raffinate and the solution boiled, the residual iridium was extracted. This peculiar behavior was attributed to one of two possibilities. First, part of the iridium had been reduced to iridium(III). The most likely source of the reducing agent was the tributyl phosphate. The extractant was purified by oxidation with permanganate and double distillation. The fraction boiling between 147–150° at 8 mm pressure was collected. Iridium still was not completely extracted with the purified solvent.

The second possibility was that the iridium existed in some form that required drastic conditions to form the extractable species. Regardless of the nature of the iridium, it was necessary to oxidize the raffinate phase after the first extraction in order to remove all of the iridium. Consequently, a countercurrent extraction was not feasible.

The selection of experimental conditions for the separation of platinum and palladium, and platinum and rhodium was based on the largest difference in distribution coefficients concomitant with minimal reagent concentrations.

The application of countercurrent distribution techniques to the problems of separations in the platinum group metals was a fresh approach to an old problem. The separations affected were quantitative, simple and fast. The ease with which the separations were affected should do much to encourage the development of similar type separations.

SUMMARY

Distribution coefficients were determined for the partitioning of the chloro-complexes of platinum, palladium, rhodium, and iridium between tributyl phosphate and various concentrations of hydrochloric acid. Theoretical calculations based on the experimentally determined distribution coefficients indicated that a seventeen stage countercurrent extraction apparatus would resolve mixtures of platinum and palladium, platinum and rhodium, and rhodium and iridium.

Mixtures of platinum and palladium, and platinum and rhodium were resolved in a fashion predicted by theory. Mixtures of rhodium and iridium were not completely resolved.

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Received October 21st, 1957

SEPARATION OF NIOBIUM AND TANTALUM WITH CUPFERRON

by

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The separation of niobium and tantalum from each other has proved to be an extremely difficult task in view of their chemical similarities, the modification of the properties of one by the presence of the other, the lack of specific reactions and their tendency to form hydrolytic products. The presence of titanium, which often accompanies these elements, renders the problem still more difficult.

The first attempt at the separation of niobium and tantalum, which was made by MARIGNAC[1], was based on the fractional crystallisation of K_2TaF_7 and K_2NbOF_5. This, however, required strictly-controlled conditions as otherwise niobium would form K_2NbF_7 and tantalum K_2TaOF_5[2].

Several modifications[3] of MARIGNAC's method were proposed, though none proved to be effective. The research of SCHOELLER *et al.*[4] on tannic acid precipitation affords a method for the determination of these metals. The method, however, is time-consuming and requires tedious fractionation of the tannin complexes precipitated from oxalic acid solution, which form a more stable niobo-oxalate complex and a less stable tantalo-oxalate. Modifications of SCHOELLER's method have been suggested. WIRTZ[5] recommended a pH of 1.9, CHARLOT AND BÉZIER[6] pH 2.2, while BHATTACHARYA[7] found pH 4.0 to be highly suitable for the complete precipitation of tantalum not contaminated with niobium, the precipitation of which began at pH 4.2 and was complete at pH 4.4. SANKAR DAS, VENKATESWARLU AND ATHAVALE[8], on the other hand, showed that niobium, tantalum and titanium, when present in a mixture, could be quantitatively precipitated together even at pH 4.0 from an oxalate solution in the presence of Complexone III, which masked the influence of most of the accompanying elements. BELEKAR AND ATHAVALE[9] recommended oxine as a precipitant for the quantitative separation of niobium from a tartrate medium at pH 6.0, and recovered tantalum from the filtrate with tannin. Titanium, if present, was found to be distributed in both fractions.

The reagent, cupferron, introduced by BAUDISH[10] for the quantitative precipitation of several elements including iron, vanadium, zirconium, titanium, tin, niobium, tantalum, uranium(IV) and presumably hafnium in strong acid solution, was found to precipitate titanium completely, even from a faintly ammoniacal solution or from a solution buffered with ammonium acetate and acetic acid, and thus could be of assistance in separating titanium[11] from quite a large number of elements masked by complexone III.

The present study of the separation of niobium and tantalum by cupferron shows that in the case of an oxalate solution both niobium and tantalum are precipitated at the same pH (2.8–5.1), whereas in that of a tartrate solution with a pH between 4.5 and 5.5 (adjusted by ammonium acetate–acetic acid buffer) niobium is completely precipitated, while tantalum remains in the solution, when the ratio of Nb : Ta in the solution is only 1 :1. Higher amounts of tantalum tend to keep the niobium in solution, but some success can be achieved by using a magnesia mixture as a coagulating agent.

The most satisfactory separation of niobium and tantalum from each other, which has been applied up to maximum ratios of 30:1 and 1:30, is effected with stannous or stannic ion used as co-precipitating agent. In this way, niobium is separated in the presence of complexone III from almost all of the elements, except uranium, beryllium, titanium and phosphate. Iron and other trivalent elements even when present in hundred-fold excess with respect to niobium, can be removed as complexes with complexone III, if necessary by double precipitation of niobium. This method, when applied to the analysis of a sample of niobium–molybdenum stainless steel, obtained from British Chemical Standards, gave very reliable results

Titanium, like tin, when present in the mixture, promotes the complete precipitation of niobium and to a much smaller extent, of tantalum, but an excess of tantalum tends to solubilize niobium salt. Coprecipitated tantalum can, however, be removed by double precipitation. Complete precipitation of niobium together with titanium is possible only when the amount of tantalum is not more than three times the amount of niobium.

EXPERIMENTAL

Apparatus

A Cambridge pH-indicator was used for the measurements of pH.

Reagents and standard solutions

The chemicals used in the investigation were all of the highest purity available.

A 0.5% solution of tartaric acid was prepared by dissolving 50 g of the acid in 1000 ml water.

Solutions of complexone III (disodium salt of ethylenediaminetetraacetic acid) and ammonium acetate were prepared separately before use, when 20 g of each were dissolved in 100 ml water.

A solution of sulphuric acid (sp.gr. 1.84), approximately 10% (w/v), was prepared by mixing 5 ml of the acid in 100 ml water.

A solution of methyl orange, 0.1 g in 100 ml water, was used as the indicator.

A suspension of paper pulp was prepared from two pieces of Schleicher and Schuell filter paper No. 589 by shaking vigorously with 30 ml boiling water.

Stannous and stannic chloride solutions were prepared from stannous chloride ($SnCl_2 \cdot 2H_2O$), 5 g of which were dissolved in 100 ml 1:1 (v/v) hydrochloric acid (sp.gr. 1.19). A portion of the solution was then oxidized to the stannic state by chlorine.

Standard solutions of niobium and tantalum were prepared from weighed amounts of their pentoxides (Specpure, Johnson and Matthey). These were fused separately with ten times their weight of sodium bisulphate and the clear melts were dissolved and made up to definite volumes in separate measuring flasks with the 5.0% solution of tartaric acid. From measured aliquot portions, the niobium or tantalum content of the respective solutions was determined by the cupferron method.

A standard solution of titanium sulphate was prepared from a weighed amount of potassium titanium oxalate by decomposing it with sulphuric acid in the presence of ammonium sulphate and diluting to the required volume. The amount of titanium per ml of the solution was estimated by the cupferron method.

Solutions of other ions were prepared from the chloride or the nitrate salts of cations and from the sodium, potassium or ammonium salts of anions. Their concentrations were determined by the standard procedure.

A 5.0% solution of cupferron (5 g in 100 ml water) prepared just before use, was used as a precipitant.

Procedure I. Magnesia mixture as a coagulating agent

To a solution of niobium and tantalum were added 10 ml of the magnesia mixture, a drop or two of the indicator, a few ml of the ammonium acetate solution until the colour of the indicator changed to yellow, and a few of the paper pulp suspension. The mixture was then diluted to 200 ml, cooled in ice and stirred while the cupferron solution was added dropwise until the precipitation of niobium was complete. The precipitate together with the paper pulp was filtered, washed with cold water, dried, ignited to Nb_2O_5 and weighed. After evaporating the filtrate to dryness the residue was first digested with fuming nitric acid and then with a mixture of perchloric and sulphuric acids in order to decompose the organic matter completely. After the fuming with sulphuric acid, the solution was cooled and diluted with water to give a solution which was 10% with respect to the acid. From this solution, tantalum was precipitated by the addition of the cupferron solution. This precipitate was then filtered, washed, dried, ignited to Ta_2O_5 and weighed. The results are given in Table I.

TABLE I

Nb_2O_5 *taken* *mg*	Ta_2O_5 *taken* *mg*	Nb_2O_5 *found* *mg*	Ta_2O_5 *found* *mg*	*pH*
4.2	4.0	4.2	—	4.5
4.0	8.0	3.8	8.0	—
4.0	12.0	colloidal	colloidal	—
10.4	10.8	10.4	11.0	4.95
10.4	21.7	9.8	22.0	5.1

When the ratio Nb:Ta was 1:1, separation without magnesia mixture was quite feasible; using the magnesia mixture, a complete separation of niobium was possible when the amount of tantalum was not more than double the amount of niobium present. Higher amounts of tantalum had a tendency to solubilize niobium and even in the presence of cupferron, rendered the precipitate colloidal.

In the presence of titanium, which itself acted as a co-precipitating agent, the above procedure, without the use of magnesia mixture, was useful for the simultaneous separation of niobium and titanium from tantalum. However, the maximum amount of tantalum that could be tolerated and be easily removed by double precipitation was only about three times the amount of niobium present in the mixture. The results are given in Table II.

TABLE II

Nb_2O_5 *taken* *mg*	TiO_2 *taken* *mg*	Ta_2O_5 *taken* *mg*	$Nb_2O_5 + TiO_2$ *found* *mg*	Ta_2O_5 *found* *mg*
10.0	9.6	5.0	19.8	5.0
10.0	9.6	10.0	19.8	9.6
10.0	9.6	15.0	20.0	14.8
10.0	9.6	20.0	20.8[a] 19.4[b]	19.8
10.0	9.6	30.0	24.0[a] 19.4[b]	29.8

[a] Single precipitation.

[b] Double precipitation.

Procedure II. With stannous or stannic ion as a co-precipitating agent

In this case, for the complete precipitation of niobium, a few drops of stannous or stannic chloride solution, instead of magnesia mixture, were added to the solution containing both niobium and tantalum. Dilution, adjustment of the pH of the solution and precipitation of the niobium were carried out as described under Procedure I. After filtration, washing and ignition to oxide the mixed precipitate of niobium and tin was fused with sodium bisulphate and the clear melt, after cooling, was dissolved in 100 ml of the tartaric acid solution. From this solution, the tin was removed by hydrogen sulphide, the excess of which was expelled by boiling, and the niobium was re-precipitated and determined according to the first procedure, without the addition of magnesia mixture or the paper pulp. The results are given in Table III.

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TABLE III

Nb_2O_5 taken mg	Sn^{+2} solution ml	Sn^{+4} solution ml	Nb_2O_5 found mg	pH
10.4	0.5	—	10.6	5.34
10.8	—	0.5	11.0	5.56
10.8	—	1.0	10.8	5.31
10.8	1.0	—	10.8	5.12

During the separation of niobium by the above procedure, it was observed that when the amount of tantalum was greatly in excess to that of niobium, the amount of stannous chloride required for the complete precipitation of niobium was about 2–3 ml and that some tin remained in solution with tantalum. With an excess of niobium, of course, the addition of only a few drops of stannous chloride was sufficient to effect complete precipitation of niobium and all the tin remained with the niobium fraction.

For the determination of tantalum, the filtrate from the niobium precipitation was evaporated to dryness and the residue was digested with nitric, perchloric and sulphuric acids, to decompose organic matter, as described under Procedure I. The solution left after fuming with sulphuric acid was cooled, diluted with the tartaric acid solution, saturated with hydrogen sulphide to remove tin and boiled to expel the excess of hydrogen sulphide. The concentration of acid in this solution was then adjusted to 10% (w/v) with sulphuric acid and the tantalum was precipitated by cupferron. The results are given in Table IV.

TABLE IV

Nb_2O_5 taken mg	Ta_2O_5 taken mg	Sn^{+2} solution ml	Nb_2O_5 found mg	Ta_2O_5 found mg
24.0	12.0	0.5	24.0	—
4.8	48.0	2.5	5.0	—
8.0	5.0	0.5	8.2	—
40.0	5.0	0.5	40.2	—
150.0	5.0	0.5	149.8	5.2
4.0	120.0	2.5	4.1	119.9
20.0	5.0	0.5	20.1	4.8

With the addition of complexone III (5 g) and tartaric acid (1 g) as complexing agents, and stannous chloride (0.5 ml) as a co-precipitant, a satisfactory separation of niobium from quite a large number of ions (except uranium, beryllium, titanium and phosphate), was possible with the second procedure. The results are given in Table V.

A Nb–Mo 18/12 stainless steel sample, No. 246, of British Chemical Standards, was analysed for its niobium content according to Procedure II and was found to give satisfactory results. The details of the procedure were as follows:

1 g of the steel was dissolved in a few ml of conc. hydrochloric acid and the solution was diluted to about 200 ml. To it were added in succession, 6–7 g complexone III, 0.5 ml stannous chloride, and a few ml of the ammonium acetate solution to adjust the pH to about 5. The solution was cooled in ice and treated with the cupferron solution, as a result of which the niobium, tin and some iron precipitated. After washing, drying and ignition to oxide, the precipitate was fused with sodium bisulphate and dissolved in tartaric acid solution. After the addition of 5–6 g of complexone III and proper adjustment of the pH, niobium together with tin was again precipitated from this solution with cupferron. This precipitate was again fused with bisulphate, dissolved in tartaric acid solution and treated in the same way as discussed above for the separation and estimation of niobium from tin. Thus, from two weighed portions, the average percentage of niobium was found to be 0.84 as compared to 0.82 stated by the British Chemical Standards.

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TABLE V

Nb_2O_5 taken *mg*	*Ions added* *mg*		*Nb_2O_5 found* *mg*
21.6	Ca	100.0	21.6
	Ba	100.0	
	Sr	100.0	
	Mg	100.0	
22.8	Zn	130.0	22.8
	Mn	130.0	
	Ni	130.0	
	Co	130.0	
22.8	As	200.0	23.0
	Sb	200.0	
22.8	Cu	100.0	23.0
	Cd	100.0	
	Hg^{+2}	100.0	
	Pb	100.0	
	Bi	100.0	
23.2	AsO_4^{-3}	100.0	23.6
	MoO_4^{-2}	100.0	
	VO_3^{-1}	100.0	
	WO_4^{-2}	100.0	
	CrO_4^{-2}	100.0	
11.0	Fe^{+3}	1000.0	74.2[a] 11.4[b]
11.0	Fe^{+3}	500.0	30.4[a] 11.2[b]
23.2	Fe^{+3}	100.0	24.0[a]
	Al	100.0	23.0[b]
	Cr	100.0	
	Th	100.0	
	Zr	100.0	
	R_2O_3*	100.0	

* R_2O_3; rare earths.

[a] Single precipitation.

[b] Double precipitation.

SUMMARY

An attempt to separate niobium and tantalum by cupferron was only moderately successful at pH 4.5 to 5.5 in the presence of a magnesia mixture as a coagulating agent. A more satisfactory separation of niobium and tantalum from each other, tried out up to ratios of 30:1 and 1:30, is effected with Sn^{+2} or Sn^{+4} as a co-precipitating agent. Under the conditions described niobium can be separated, in the presence of complexone III, from almost all the ions except U, Be, Ti and PO_4^{-3}. Iron and other tervalent elements, when present in 100 fold excess with respect to niobium, require double precipitation. The method gives highly satisfactory results when applied to the analysis of niobium in niobium–molybdenum stainless steel.

The use of titanium as a co-precipitant is less successful than that of tin.

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Received October 24th, 1957

SEPARATION OF NIOBIUM AND TANTALUM WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

by

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Recently, MAJUMDAR AND RAY CHOWDHURY[1] proposed a method for the separation of niobium from tantalum and of niobium from most other elements. The separation was carried out from tartrate medium buffered with ammonium acetate (pH 4.5 to 5.5), with or without complexone III as the masking agent, using cupferron as the precipitant for niobium, and tin as co-precipitant. A highly satisfactory separation was obtained when the elements were present in different ratios, at least up to ratios of 1:30 and 30:1; niobium could be separated from almost all the ions except uranium, beryllium, titanium and phosphate. Iron and other trivalent elements, when present in excess, required double precipitation of niobium.

The effectiveness of cupferron prompted the authors to investigate the behaviour of its derivatives, one of which is N-benzoyl-N-phenylhydroxylamine. When this is used as a precipitating agent, niobium can be estimated in a tartrate solution maintained at an acidity of 2.0*N* and the pH range of precipitation can be extended up to a maximum of about 6.5. Complete precipitation of tantalum is possible below pH 1.5 and even at an acidity of 2.0*N*; a higher pH tends to keep the tantalum in solution. Within the pH range 3.5 to 6.5, niobium is completely precipitated while tantalum remains in solution; the latter is then precipitated by acidification. A single precipitation is sufficient for the estimation of niobium and tantalum in mixtures with ratios Nb:Ta between 1:16 and 100:1. Even when this ratio is 1:100 the determination can still be carried out by precipitating twice. In the presence of complexone III and tartaric acid, the separation of niobium from other ions, *e.g.*, ferric, uranyl, beryllium, thorium, chromic, aluminium, cerous, ceric, cupric, cadmium, bismuth, lead, mercuric, arsenious, antimonious, stannic, zinc, manganous, nickel, cobaltous, calcium, strontium, barium, magnesium, phosphate, chromate, tungstate and arsenate ions and those of rare earths is achieved. The precipitate of tantalum is less granular than that of niobium though it can be easily filtered and washed. The time taken for the entire procedure, including the weighings of the ignited pentoxides, is much less than is required by any other method.

While this work was in progress, it was brought to our notice that MOSHIER AND SCHWARBERG[2] had published a paper on the use of this hydroxylamine reagent for the determination of tantalum in the presence of niobium in a ratio of about 5:1. This method involves precipitating at least twice from a hydrofluoric acid–sulphuric acid solution at pH 1.0. The method works well, as was indicated, for the estimation of tantalum only when precipitation is carried out at room temperature and the product is digested on a tap waterbath for 2.5 hours.

N-Benzoyl-N-phenylhydroxylamine was introduced as a reagent by BAMBERGER[3] and utilized by SHOME[4-6] for the gravimetric determination of titanium, iron, aluminium and copper and the colorimetric determination of vanadium, and because of its stability to heat and light, it was recommended as superior to cupferron.

EXPERIMENTAL

The chemicals and solutions employed were identical with those previously used by one of the present authors[1].

Standard solutions of niobium and tantalum

A weighed quantity of niobium or tantalum pentoxide (Specpure, Johnson and Matthey) was fused in a silica crucible with ten times its weight of potassium bisulphate (G.R., E. Merck), extracted with a 5% (w/v) tartaric acid solution and made up to a definite volume with water. The niobium or the tantalum content was determined by estimating it from an aliquot portion of the solution with cupferron[7].

Reagent

Nitrobenzene was first reduced by zinc[8] to phenylhydroxylamine, which was then converted to N-benzoyl-N-phenylhydroxylamine according to the procedure suggested by SHOME[6]. A 10% (w/v) alcoholic solution of this product (m.p. 120-121°) was used as a reagent for the precipitation of niobium and tantalum.

Wash water

0.1 g of the reagent was dissolved in 100 ml of boiling hot water.

Apparatus

A Cambridge pH indicator was used for all pH measurements.

Effect of pH

An aliquot of the standard solution of niobium or tantalum was taken and its pH adjusted to a desired value either by dilute sulphuric acid or by a 20% (w/v) ammonium acetate solution; the solution was diluted to about 200 ml. A pH above 5.9 was attained by adding a few drops of dilute ammonia after the ammonium acetate. The reagent was added to the hot solution slowly, while stirring, until a white turbidity appeared. The mixture was kept on a boiling waterbath for about 45 min with occasional stirring to coagulate the precipitate. This was then filtered, washed with wash water, dried, ignited and weighed as the pentoxide. The precipitation of niobium is quantitative up to a maximum pH of 6.5 and that of tantalum up to only pH 1.5. At higher regions low results are usually obtained owing to incomplete precipitation.

TABLE I

pH RANGE OF COMPLETE PRECIPITATION

Nb_2O_5			Ta_2O_5		
taken mg	*found mg*	*pH*	*taken mg*	*found mg*	*pH*
4.95	5.1	a	12.8	12.6	a
13.80	13.70	0.5	9.6	9.4	0.4
13.80	13.60	2.0	9.6	9.6	1.2
13.80	13.60	3.1	9.6	9.4	1.5
13.80	13.70	3.9	9.6	8.4	1.8
13.80	13.60	4.7	9.6	6.6	2.5
10.20	10.30	5.5	9.6	2.4	3.0
10.20	10.20	6.5	9.6	Nil	3.5
10.20	8.9	6.9			
10.20	8.3	7.2			
10.20	4.6	8.2			
10.20	1.4	8.9			

[a] Solution 2.0N with respect to sulphuric acid.

Separation of niobium and tantalum

Aliquots of standard solutions of niobium and tantalum were mixed and the pH of the solution was adjusted by ammonium acetate solution to any value between 3.5 and 6.5 (preferably to pH 6.0 to avoid contamination by tantalum when this is present in high excess). The solution was diluted to about 350 ml, heated to boiling, and the niobium precipitated with the reagent and converted to oxide for weighing as described above. From the mixed solution of the filtrate and the washings, the tantalum was precipitated simply by the addition of dilute sulphuric acid to lower the pH to about 1.0. This mixture was heated to boiling and kept on the boiling waterbath for about 45 min. The resulting precipitate was filtered, washed, ignited and weighed as in the case of niobium. The results are given in Table II.

TABLE II

SEPARATION OF NIOBIUM AND TANTALUM

Nb_2O_5 *taken* *mg*	Ta_2O_5 *taken* *mg*	*pH for Nb precipitation*	*pH for Ta precipitation*	Nb_2O_5 *found* *mg*	Ta_2O_5 *found* *mg*
10.2	10.4	5.0	0.5	10.0	10.6
10.2	52.0	5.7	0.5	10.0	51.8
10.2	104.2	5.6	0.5	10.2	103.8
10.2	160.0	5.7	0.7	10.4	159.8
10.2	172.8	5.6	0.6	11.2	171.6
4.3	103.7	5.8	0.5	11.4[a]	96.8[a]
				4.1[b]	7.2[b]
4.3	123.7	5.8	0.5	12.0[a]	115.8[a]
				4.2[b]	7.6[b]
5.2	290.2	5.9	0.6	15.0[a]	280.0[a]
				5.4[b]	9.6[b]
2.6	276.2	5.9	0.6	10.6[a]	268.4[a]
				2.6[b]	7.6[b]
80.1	4.2	5.7	0.8	79.8	4.3
202.4	4.2	5.8	0.8	202.2	4.4
402.4	4.2	5.9	0.6	403.0	3.8

[a] Single precipitation.
[b] Double precipitation.

When the ratio Nb_2O_5 to Ta_2O_5 was within the range 1:16 to 100:1, a single precipitation was sufficient for the complete separation of niobium and tantalum; for higher ratios up to 1:100, however, a second precipitation was necessary for niobium.

When less than 5 mg of niobium or tantalum was present, paper pulp was used to aid the filtration. The presence of a large excess of tantalum or complexing agents, *e.g.* complexone III and tartaric acid, made a longer period of about 90 min necessary for complete coagulation of the niobium precipitate.

Effect of various ions

Excesses of tartaric acid and complexone III, in quantities two to three times the theoretical amount of the various ions, were added in succession to the solution. Niobium then was estimated after the proper adjustment of pH from 3.5–6.5 by the procedure given above. Table III shows that with the exception of titanium, zirconium, vanadate and molybdate, all other elements tested remained in solution under the experimental conditions.

TABLE III

Nb_2O_5 taken mg	*Ions added mg*		*Nb_2O_5 found mg*
19.8	Fe^{+3}	224.0	19.6
19.8	Fe^{+3}	560.0	19.7
19.8	U	120.0	19.6
	Be	120.0	
	Th	120.0	
19.8	Cr	100.0	20.0
	Al	100.0	
	R.E.	100.0	
	Ce^{+3}	100.0	
	Ce^{+4}	100.0	
9.9	Cu	100.0	10.0
	Cd	100.0	
	Bi	100.0	
	Pb	100.0	
	Hg	100.0	
19.8	Zn	100.0	19.4
	Mn	100.0	
	Ni	100.0	
	Co	100.0	
19.8	As	100.0	20.0
	Sb	100.0	
	Sn	100.0	
19.8	Ba	100.0	20.2
	Ca	100.0	
	Sr	100.0	
	Mg	100.0	
9.9	PO_4^{-3}	100.0	9.8
4.95	WO_4^{-2}	125.0	5.0
4.95	CrO_4^{-2}	120.0	5.0
4.95	AsO_4^{-3}	130.0	4.9

R.E. = Rare earths

SUMMARY

The use of N-benzoyl-N-phenylhydroxylamine for the separation of niobium and tantalum, allows a satisfactory estimation of niobium from a tartrate solution at an acidity of 2.0*N*. The pH range for complete precipitation can be extended to 6.5. For tantalum precipitation, the pH of the solution should be below 1.5 and the acidity may even be above 2.0*N*. At pH 3.5–6.5, niobium is completely precipitated and tantalum remains in solution; the latter is precipitated by lowering the pH. Niobium and tantalum in ratios of 1:16 to 100:1 can be separated by a single precipitation, in the case of a ratio of 1:100 precipitation must be carried out twice. Titanium, zirconium, vanadate and molybdate interfere with the determination of niobium though other ions have no effect in the presence of complexone III and tartaric acid. The precipitates are granular and easy to filter and wash. The time taken for a complete analysis is much less than that of other methods.

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Received October 24th, 1957

THE FERRIC HYDROXAMATE COLOUR REACTION
II. THE SPECTROPHOTOMETRIC DETERMINATION OF ACETIC ANHYDRIDE

by

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A previous report[1] has described the direct titration of hydroxyl groups with acetic anhydride in the presence of perchloric acid using the formation of ferric acetohydroxamate, $Fe(CH_3CONHO)_3$, as external indicator. The deep-red colour of the complex ferric salt and the facility with which it is formed suggested that in it might be found the basis of a convenient spectrophotometric determination of acetic anhydride and hence of hydroxyl groups. Related spectroscopic methods have been described: esters[2,3] have been determined first by conversion to hydroxamic acids and then to the corresponding ferric salt and a micro-method for the detection and estimation of hydroxylamine[4] is based on the formation of ferric formohydroxamate. Any detailed examination of these reactions has been made difficult by their necessarily energetic conditions. The largely different and milder conditions used in the present investigation proved more amenable to such an examination.

EXPERIMENTAL

Reagents

Solutions of ferric chloride (anhydrous) (1.5 g) in ethanol (250 ml) and hydroxylamine hydrochloride (30 g) in methanol (250 ml) were stored in dark bottles. Although they appeared to be stable for several weeks, fresh solutions were prepared every two days. A solution of perchloric acid in acetic acid was prepared from 60% perchloric acid[1] and diluted with acetic acid to make the perchloric acid 0.1 *N*. Acetic anhydride was diluted with acetic acid or with ethyl acetate. All reagents, except ferric chloride, were of AnalaR quality.

Spectral measurements

Spectra were determined on a Beckman DU spectrophotometer. Methanol was used throughout as the liquid in the blank cell. The spectrum of the complex showed a broad band, λ_{max} 520 mμ. To determine the course of the reaction, optical densities were measured at 520 mμ.

Procedure

Two methods of performing the reaction were adopted: one designed to show most simply the effect of the variables on colour formation, the other to approximate closely to conditions more convenient for the determination of acetic anhydride in the estimation of hydroxyl groups. (i) Ferric chloride solution (10 ml) was diluted with hydroxylamine hydrochloride solution (2 ml) and then allowed to stand (T_1 minutes). Perchloric acid (10 ml) was added and the solution again allowed to stand (T_2 minutes). Acetic anhydride was added and after a further period (T_3 minutes) the solution was diluted with water (3 ml). Spectral measurements were made after a further incubation period (T_4 minutes). (ii) To a mixture of the solutions of ferric chloride (10 ml) and hydroxylamine hydrochloride (2 ml) which had been allowed to stand (T_1 minutes), perchloric acid (10 ml), previously mixed and allowed to stand with acetic anhydride (T_5 minutes), was added. The combined solutions were allowed to equilibrate (T_6 minutes) and then the solution was diluted with water (3 ml). The spectral measurements were made after a further period (T_4 = 25 minutes).

The time factors (T_{1-6}) and the concentrations of hydroxylamine, perchloric acid, acetic acid, acetic anhydride, and water were varied systematically. In all experiments there was an excess of ferric ions.

RESULTS

Preliminary results had indicated that only under carefully defined conditions could the formation of ferric acetohydroxamate be rendered reproducible. It was anticipated that decomposition of the derivatives of the hydroxamic acid and redox reactions involving ferric salts would be responsible for most of the complications. These expectations were partially fulfilled.

Interaction between hydroxylamine and iron salts can lead to both oxidation and reduction[5]. In alkaline solution hydroxylamine is capable of oxidising ferrous to ferric; under acidic conditions the reverse reaction has provided the basis for an analytical method. In aqueous solution the reaction is fast even at room temperature[6], but in methanol it is sufficiently slow to prevent it influencing the formation of ferric acetohydroxamate: varying the time of interaction of the solutions of ferric chloride and hydroxylamine (T_1) had no effect on the observed optical density of the complex. Equally without effect on the formation of the complex was the time of interaction of acetic anhydride and perchloric acid (T_5).

However, when perchloric acid was added to premixed ferric chloride and hydroxylamine, an increase in the period of equilibration (T_2) was accompanied by an increase in the optical density of the hydroxamate complex (Fig. 1). It seems possible that this is due to a slow change or series of changes amongst the ferric ions present in solution. It is to be expected[7] that the principal ferric ions in the solution of ferric chloride and hydroxylamine hydrochloride will be $FeCl_2^+$ and $FeCl^{+2}$. Addition of perchloric acid to the solution will displace the equilibria towards the more highly charged ions and the solution will become further complicated by the presence of acetate and perchlorate[8] complexes. The equilibria which are slowly established among these ions must favour those which eventually react more readily with acetohydroxamic acid. On

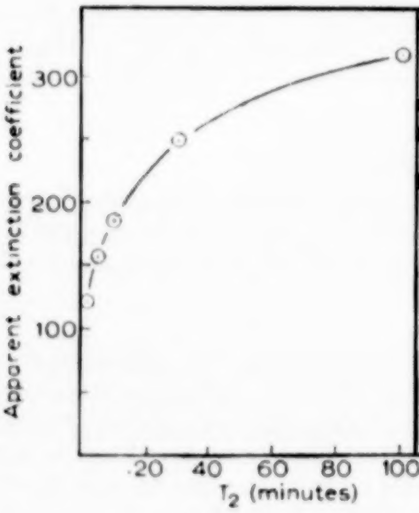

Fig. 1.

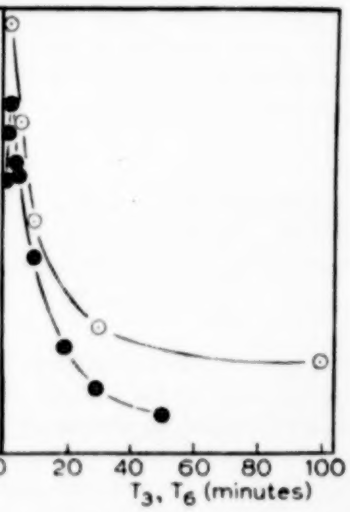

Fig. 2.

Fig. 1. Effect of varying time of interaction of perchloric acid with $FeCl_3/NH_2OH$
$T_1 = 10, T_3 = 10, T_4 = 25; [(CH_3CO)_2O] = 4.26 \cdot 10^{-3} M$

Fig. 2. Effect of varying time of interaction of acetic anhydride with $HClO_4/FeCl_3/NH_2OH$.
⊙ $T_1 = 10, T_2 = 10, T_3$ varied, $T_4 = 25; [(CH_3CO)_2O] = 4.26 \cdot 10^{-3} M$
● $T_1 = 5, T_5 = 10, T_6$ varied, $T_4 = 25; [(CH_3CO)_2O] = 5.41 \cdot 10^{-3} M$

general grounds, it seems more likely that this will be true for the more highly charged cations but on the present evidence it is clearly not profitable to attempt further to correlate this reactivity. A converse effect is shown when the incubation period of solutions which contain all the reagents except water (T_3, T_6) is increased: the observed optical density shows a marked decrease (Fig. 2). At this stage the reaction mixture is the familiar pale-yellow colour of the so-called ionic ferric complexes. The deep-red ferric hydroxamate complex is not observed until water has been added to this solution. It seems therefore that in the absence of water either hydroxamic acids do not enter into combination with the ferric ions present in the reaction solution or that the absorption band at 520 mμ characteristic of the complex is inhibited. The strongly coloured solutions given by ferric acetohydroxamate in non-aqueous solvents[9] render the second alternative so remotely possible that it can be dismissed. The decreased efficiency of the reaction when solutions are allowed to stand for long periods before water is added may well be ascribed to decomposition of the hydroxamic acid. Although formation of the hydroxamic acid occurs preferentially, it may well suffer an acid catalysed alcoholysis:

$$CH_3CONHOH + H^+ \rightarrow CH_3CO^+ + NH_2OH$$

$$CH_3CO^+ + CH_3OH \rightarrow CH_3COOCH_3 + H^+$$

It is possible that the acid catalysed hydrolysis of hydroxamic acids[10] proceeds by a similar mechanism. By removing part of the hydroxamic acid before it is stabilised by combination with ferric ion, such a reaction would lead directly to a decrease in the intensity of colour due to the salt.

The addition of water to the reaction mixture causes gradual development of the colour. It may be assumed that a further change in the equilibria among the ferric ions occurs during the formation of the complex salt; the apparently selective nature of the hydroxamate ligand may well arise from its bidentate form. The rate of formation of the ferric complex is governed partly by the amount of water which is added (Fig. 3). The development of colour, slow in the presence of low concentrations of water, is increased to a maximal value as the water content rises. Above this value, further dilution causes sufficient reduction in the acidity to permit rapid fading (see below).

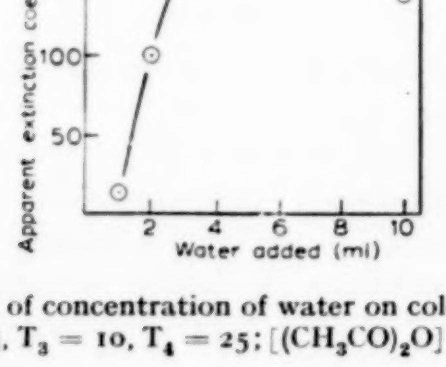

Fig. 3. Effect of concentration of water on colour formation.
$T_1 = 5$, $T_2 = 5$, $T_3 = 10$, $T_4 = 25$; $[(CH_3CO)_2O] = 4.26 \cdot 10^{-3} M$.

Preliminary results had indicated that the colour of the complex in neutral solutions was both more intense and more transient than that found in the strongly acidic reaction solutions. A more detailed examination confirmed these results (Fig. 4). A smooth transition from an asymptotic curve in strongly acid solution to a sharply peaked curve of higher intensity in neutral solution was observed. Two factors appear to be responsible for this transition. The weakening of the absorption may be due to protonation of the hydroxamate group, potentially basic under strongly acidic conditions. The increased rate of decay as the acidity decreases, may be ascribed to reduction of the ferric complex by hydroxylamine. Support for this hypothesis was provided by increasing the concentration of hydroxylamine hydrochloride. It was found (Fig. 5) that this exerted only a minor effect on the maximum intensity of the absorption, but the rate of decay of the colour was significantly increased. It appears that reduction of the protonated complex is less readily accomplished than is that of the neutral salt.

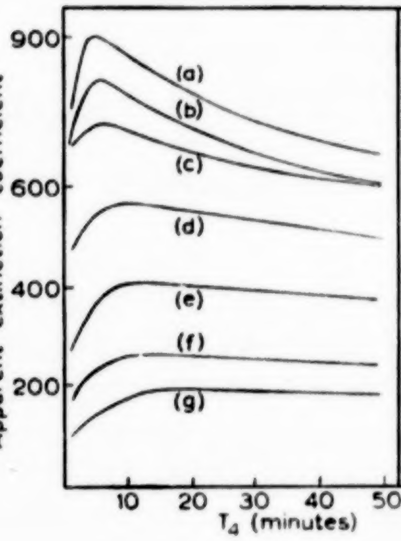

Fig. 4.

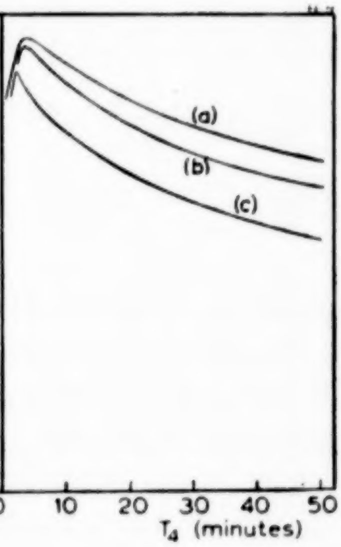

Fig. 5.

Fig. 4. Effect of acidity on colour formation.
$T_1 = 5$, $T_2 = 5$, $T_3 = 10$; $[(CH_3CO)_2O] = 1.70 \cdot 10^{-3} M$.
Perchloric acid solution in the reaction mixture was replaced by: (a) 10 ml methanol; (b) 9 ml methanol + 1 ml acetic acid; (c) 5 ml methanol + 5 ml acetic acid; (d) 10 ml acetic acid; (e) 8 ml acetic acid + 2 ml 0.1*N* perchloric acid; (f) 5 ml acetic acid + 5 ml 0.1*N* perchloric acid; (g) 10 ml 0.1*N* perchloric acid.

Fig. 5. Effect of hydroxylamine on colour formation.
$T_1 = 5$, $T_2 = 5$, $T_3 = 10$; $[(CH_3CO)_2O] = 1.70 \cdot 10^{-3} M$.
Perchloric acid solution in the reaction mixture was replaced by: (a) 10 ml methanol; (b) 9 ml methanol + 1 ml hydroxylamine solution; (c) 5 ml methanol + 5 ml hydroxylamine solution.

CONCLUSIONS

The formation of ferric acetohydroxamate is revealed as a reaction sensitive to changes in the conditions: the observed optical density depends sharply on the time factors T_2 and T_3 or on T_6 (it may be noted that errors in times T_2, T_3 if both are of the same sign, will tend to cancel each other). In this it is not ideally suited to analytical application. However, control of the factors leading to the variations can readily be achieved. Under such conditions the results are precisely reproducible and the colour reaction may be shown to obey Beer's Law accurately up to a concentration of $5 \cdot 10^{-3} M$. Together with the simplicity of the method and the ready availability of the reagents, this suggests that procedure may prove convenient for the direct estimation of acetic anhydride and the indirect estimation of acylable hydroxyl groups. To exemplify this, solutions of water, methanol, ethanol, and propanol in acetic acid, each containing $5 \cdot 10^{-5}$ moles of acylable hydroxylic compound, have been determined with an accuracy of better than 2% by interpolation on a calibration curve similar to those of Fig. 6. Further investigation is being undertaken of the complexity both of the reactions leading to the formation of the hydroxamate salts and of the equilibria among the ferric ions.

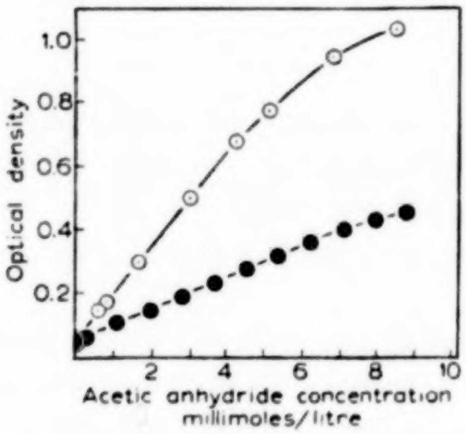

Fig. 6. Beer's Law.

⊙ $T_1 = 5$, $T_2 = 5$, $T_3 = 10$, $T_4 = 25$;
● $T_1 = 5$, $T_5 = 10$, $T_6 = 20$, $T_4 = 25$.

ACKNOWLEDGEMENTS

This work was performed during the tenure of a Civil Service Senior Research Fellowship. The author has to thank the Chief Scientist, Ministry of Supply for permission to publish these results.

SUMMARY

The conditions necessary for the formation of ferric acetohydroxamate to be used as a spectrophotometric method have been investigated and shown to be capable of control. The reaction is complicated by the complex equilibria among the ferric ions and by the limiting stability of the hydroxamate system. The use of the method in the determination of hydroxylic compounds is illustrated.

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Received September 30th, 1957

ON THE HETEROMETRIC TITRATION OF SMALL AMOUNTS OF SULFATES

by

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INTRODUCTION

At the time of the publication in this journal of a paper by BOBTELSKY AND EISENSTADTER[1], concerning the heterometric titration of sulfates, we were already engaged in a similar investigation. Since our results do not fully coincide with those of BOBTELSKY, it seems advisable to publish them, even though our procedure is similar to his in some respects.

The rapid estimation of small amounts of sulfate, preferably by means of titrimetric methods, has been the subject of innumerable publications. Nevertheless, a really satisfactory solution of the problem has not as yet been given. The many "classical" titrations, both alkalimetric and iodometric, are rather laborious and inaccurate, especially for small amounts of sulfate. The more recent titrations with Ba^{+2} solutions, either with complexone, or using sodium rhodizonate or tetrahydroxyquinone as an indicator, are either inaccurate or else require a very special illuminating apparatus. Moreover, they are subject to serious interference by foreign anions. Absorption indicators, as recently advocated by FRITZ *et al.*[2,3] and WAGNER[4], require a good deal of experience before yielding satisfactory results and even then are only useful in fairly concentrated solutions.

A number of investigators[5,6] have recommended nephelometric determinations. However, unless rather complicated and expensive apparatus is used, the measurement of scattered light is far less accurate than the measurement of transmitted light. Therefore, in principle, turbidimetric methods are to be preferred. In order to prevent misunderstanding, we prefer to use the designation "*heterometric methods*" as advocated by BOBTELSKY[15] and his co-workers.

Of course, the estimation of sulfates by titration with a Ba^{+2} solution and measurement of the transmitted light, is far from new. A fundamental study of it was published as long ago as 1941 by RINGBOM[7]. Since then — and even before that time — many analysts have occupied themselves with the subject, using either Ba^{+2} solutions[8–13] or Pb^{+2} solutions[14].

From all this work, it was concluded that it is necessary to add alcohol to the solution in order to make the precipitation of barium sulfate reasonably complete in dilute solutions. According to most investigators, it is highly desirable to add a protective colloid also. As far as we know, only CHEPELEVETSKII *et al.*[11], FREY[12] and BOBTELSKY *et al.*[1] dispensed with this colloid. Indeed, the addition of such a colloid, *e.g.* gelatine, agar, gum arabic, carboxymethylcellulose, is in itself a drawback for work on a micro scale if only because the colloid introduces traces of sulfate foreign to the sample.

The Russian investigators[10] worked with far more concentrated solutions than held our interest; nor did they add alcohol. The work of TANANAEV *et al.*[12] is mostly a study of the influence of the ethanol content and of the effects caused by the addition of $BaCl_2$ and NaCl. The Japanese investigators[14] used Pb^{+2} solutions, which we find objectionable since these are far more liable to interference by foreign anions. Only the work of FREY[13] is more or less comparable to our own. Even so, like BOBTELSKY, he restricts himself to the addition of ethanol, whereas our own work started with a study in which the addition of higher alcohols, either with or without ethanol, was investigated.

EXPERIMENTAL

From the very beginning it seemed desirable to reduce the apparatus to the utmost simplicity in order to arrive at a method of the widest applicability. At the same time we were always aware of the importance of very efficient stirring, which for work on a micro scale meant magnetic stirring. These considerations led us to the apparatus shown in Fig. 1.

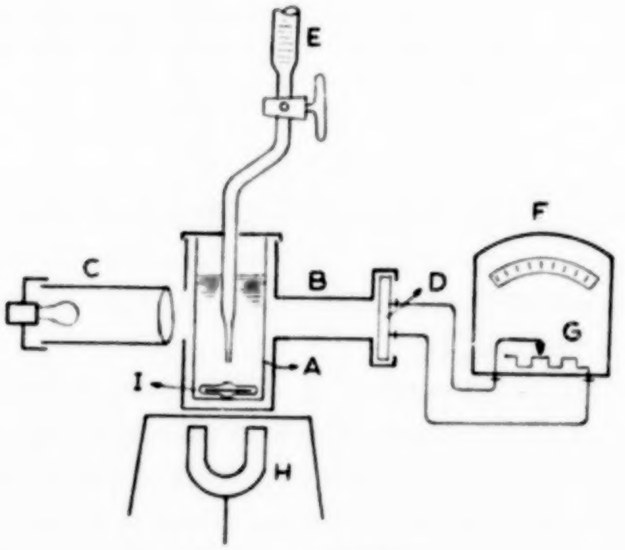

Fig. 1. Apparatus.

A is the cuvette, measuring 20 × 40 × 50 mm internally. In order to exclude stray light, it is encased in a metal holder B with a cap and hole through which the fine tip of the burette E is introduced into the liquid. The holder B also carries photocell D (Megatron A), connected to a sensitive and stable galvanometer F ("EEL", full-scale 7.5 μA, 2000 Ω) and an adjustable shunt of about 1000 Ω which served to regulate the sensitivity of the box galvanometer. H is the rotating magnet, which operates the *two* stirrers I in the cuvette. The light source is a lamp C (6 V, 5 A) placed in the focus of a lens so that a parallel beam of light is incident on the cuvette and photocell. A long neck (16 × 40 mm) on the metal holder eliminates any stray illumination on the photocell. The whole apparatus can easily be built from normal laboratory equipment. Only the metal holder had to be specially made.

The operation of the apparatus is simple. A sample of the sulfate solution is brought into the cuvette, the required amounts of water and alcohols are added (ensuring that the level of the liquid is well over the neck of the holder), the pH is adjusted to the right value, two microstirrers are placed in position, the cuvette is placed in the holder, and the cap is put on. The shunt is then adjusted so that the galvanometer deflection is nearly full-scale. Before starting the titration, it is desirable to stir for about one minute and then turn off the stirrer. Any air bubbles clinging to the stirrer or cuvette can be removed with a thin glass rod. The tip of the burette is introduced into the solution, burette and galvanometer are read, and the tiration begins. Small quantities of a standardized Ba^{+2} solution are added and the burette and galvanometer are read after each addition. The accuracy of the titration is essentially increased by waiting the

the same length of time, say 0.5 to 2 min, between the addition and the reading of the galvanometer. The slower the titration is carried out, the more accurate are the results. If the amount of sulfate present is approximately known, one can proceed with fairly large additions, decreasing their size as the end-point is approached. The end-point is indicated by the fact that the galvanometer readings either increase, remain the same, or at least decrease far more slowly. In order to obtain clear titration curves, it is advisable to continue the addition of reagent until an excess of about 35% has been added.

As a reagent aqueous barium nitrate solution was generally used. Barium nitrate is easily obtained in a pure state and can be dried at about 100° exactly to anhydrous barium nitrate. The concentration of the reagent solution must be adapted to the amount of sulfate being determined. As a rule was used $M/50$ solutions for amounts of sulfate ranging from 2 to 10 mg.

Since, at all costs, the precipitation of other barium salts must be prevented, the work was always performed in slightly acid solution. A pH of 1.5 was obtained by adding thymol blue as an indicator and acidifying to a pinkish color by addition of $2N$ HCl. Should the sample be more acid to begin with, aqueous ammonia can be added until the same color is attained. A pH of 1.5 is adequate to prevent the hydrolysis of salts of iron, aluminium, etc., if these are present, and it considerably increases the solubility of calcium sulfate. From a great many investigations on the gravimetric determination of sulfate as barium sulfate, it is well known that 0.02–0.03N HCl is the upper limit of acid concentration which allows a practically complete precipitation.

The construction of the tiration curve can be done by calculating the optical density or extinction from the galvanometer readings. This seemed to us to be an unnecessary step. The galvanometer readings were always plotted directly against the burette readings and this procedure was found to be perfectly satisfactory.

When, during the titration, the galvanometer readings attain values below about 40% of the original full-scale reading, it is desirable to bring the galvanometer again to full-scale by increasing the shunt resistance. Only readings taken after this adjustment need be plotted for the construction of the titration curve.

RESULTS

We first of all ascertained the effect of the addition of alcohols other than ethanol. These included methanol, isopropanol, and *n*-butanol. Since the latter is not sufficiently miscible with water to be used alone, it was always used in conjunction with one of the other alcohols.

Typical titration curves are shown in Fig. 2. They show only the parts of the curves in the neighborhood of the end-point, which in all cases should be 5.00 ml. Galvanometer readings have been shifted in order to get all of the curves on a single diagram. One division on the galvanometer axis is always equal to ten scale divisions, starting from the full-scale value of one hundred. All the titrations whose curves are shown in Fig. 2 were carried out on 5 ml of an aqueous $M/50$ solution of potassium sulfate. This volume contained about 10 mg of sulfate ion. To this sample were added 5 ml of double-distilled water and 14 ml of one of the alcohols or alcohol mixtures. After the pH was adjusted as described above, the solution was titrated with an aqueous $M/50$ barium nitrate solution. The alcohol concentration at the end-point, was then always about 50% by volume.

Curves a and a′ resulted from methanol, b and b′ from ethanol, c and c′ from isopropanol, and d and d′ from a mixture containing ethanol and *n*-butanol. This mixture was composed of ethanol, *n*-butanol, and water in the ratio of 1:1:2. Curves e and e′ resulted from equal volumes of isopropanol and *n*-butanol. Curve f, which resulted from a titration performed in pure water, is given for comparison.

The most striking result shown in Fig. 2 is that of all the alcohols, ethanol is the least appropriate for this titration. Curves b and b′ are rounded off at the end-point, so that the point of intersection cannot be exactly located. Isopropanol (curves c and c′) is slightly better, but still somewhat rounded. Methanol (curves a and a′) gives exemplary curves, practically straight lines, but the points of intersection are slightly low, being at about 4.93 ml instead of 5.00 ml. Moreover, methanol is less desirable in view of the insolubility of calcium sulfate in methanol–water mixtures, which may easily lead to complications whenever very small amounts of Ca^{+2} are present.

The best results were obtained with a mixture of ethanol and *n*-butanol (curves d and d′). The curves are practically straight lines and the points of intersection are quite close to the calculated value. They are 4.98 and 5.00 ml. With other concentrations of the sulfate solution, we likewise found the ethanol-*n*-butanol mixture the most appropriate.

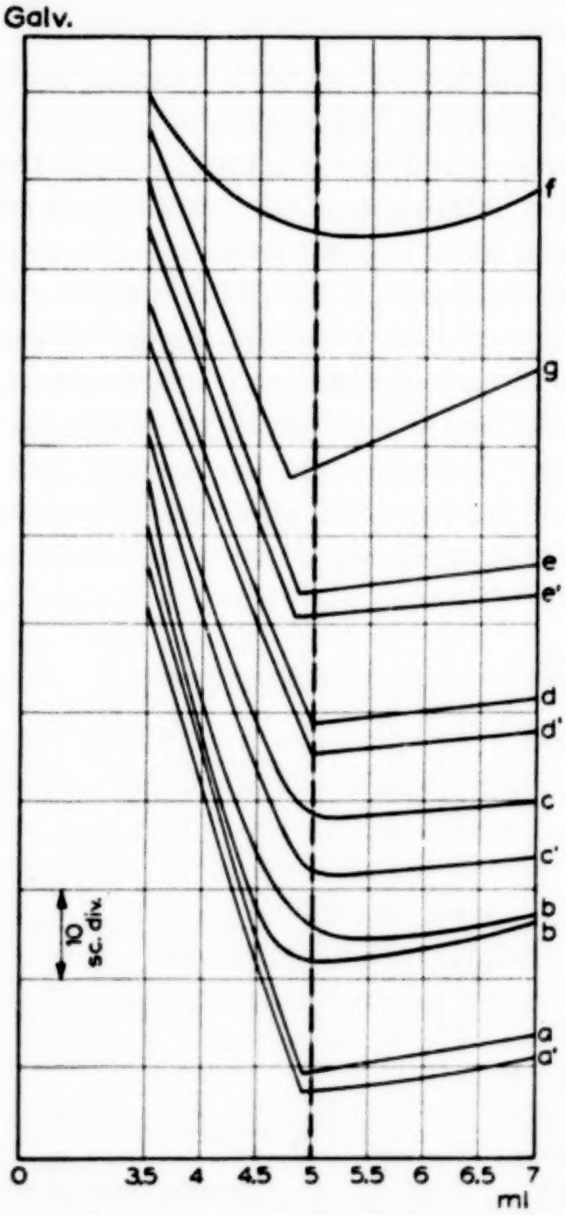

Fig. 2. Titration curves in different alcoholic media.

Curves d and d′ show at the same time that it is not necessary to add a protective colloid. Indeed, so long as there is no more than about 20 mg of sulfate in about 30 ml of solution in the cuvette, the suspension of barium sulfate is completely homogeneous. Only when the amount is greater than 20 mg in a like volume does a perceptible "clouding" occur which gives rise to unsteady galvanometer readings. We even found the addition of the colloid to be detrimental. As often as not, the colloid flocculated in 50% alcohol (*e.g.* gum arabic and carboxymethylcellulose) and the point of intersection of the curves became decidedly less exact. The last curve, g, in Fig. 2 illustrates the result of a titration of the usual amount of sulfate in water, ethanol, *n*-butanol, to which 5 mg of gelatine had been added. The end-point is clearly less exact than the same titration performed without the gelatine (d and d'). Presumably, this result, so strikingly at variance with those of earlier investigators, must be attributed to the fact that modern magnetic stirring is much superior to older procedures.

The reproducibility attained with about 10 mg of sulfate, was about ± 1%. Although the accuracy of both the burette and galvanometer readings is far better than 1%, there remains a certain fluctuation in the results which we cannot explain.

Up to this point, all the titrations had been carried out on about 10 mg of sulfate, *i.e.*, 5 ml of $M/50$ potassium sulfate, 5 ml of water, 7 ml of ethanol, 7 ml of *n*-butanol, and, at the end-point, about 5 ml of the $M/50$ barium nitrate titrant. Thus, there was about 50% alcohol by volume at the end-point. When we began to work with larger quantities of sulfate, 20 mg, with no extra water or alcohol, and using the same titrant, we found distinctly low results as shown in curve h of Fig. 3. The errors were $-1\frac{1}{2}$ and $-2\frac{1}{2}$%, respectively. We ascribe this result to the fact that, since 10 ml of titrant were now needed, the alcohol concentration at the end-point was well below 50%. Indeed, when we titrated the same solution with an aqueous

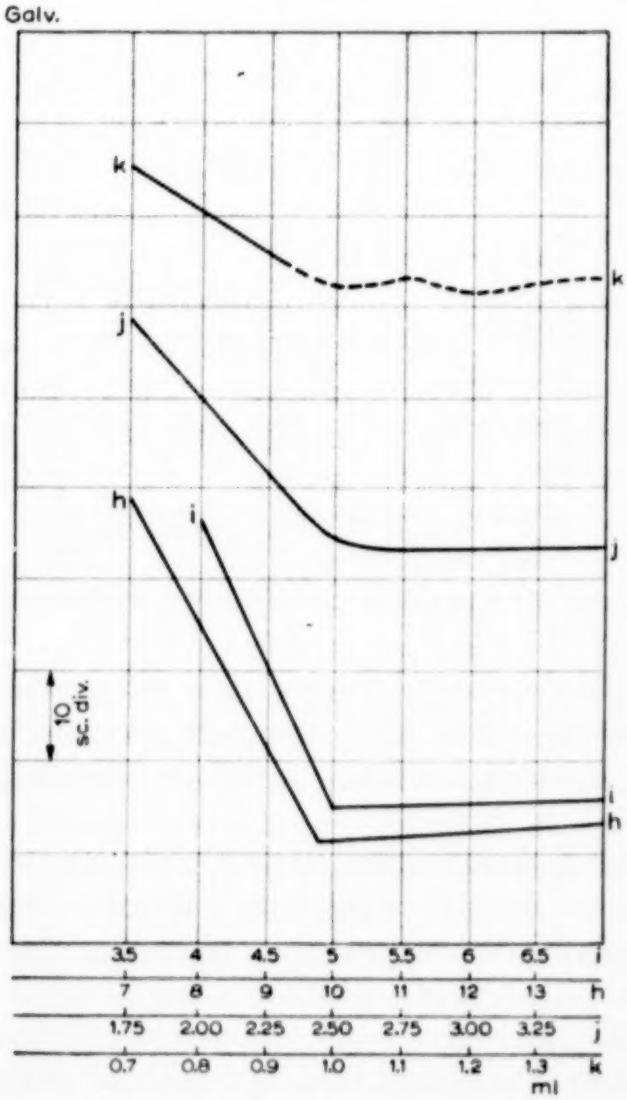

Fig. 3. Titration curves of different amounts of sulfate.

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barium nitrate solution having a concentration of $M/25$, so that the amount needed was again about 5 ml, we obtained exactly the correct end-point (error less than $\frac{1}{2}\%$). The curve for this titration is shown as curve i in Fig. 3. It seems necessary, then, when working with more than 10 mg of sulfate, to adapt the concentration of the titrant to the amount of sulfate. Of course, a barium nitrate solution in a water-alcohol mixture may be used.

For less than 10 mg of sulfate in 10 ml of water, this complication does not arise. A slight excess of alcohol at the end-point is far less detrimental than a shortage. Curve j of Fig. 3 gives the result from 2.50 ml of $M/50$ potassium sulfate (*i.e.* about 5 mg sulfate), 7.5 ml of water, 7 ml of ethanol, and 7 ml of *n*-butanol. Curve k shows the result from the titration of 1.00 ml of the potassium sulfate solution (*i.e.* about 2 mg sulfate), 9 ml of water and the same quantities of alcohol. Both were titrated with $M/50$ aqueous barium nitrate. The curves show that the point of intersection now becomes less sharp, although it is found in approximately the right place. Particularly the curve for 2 mg (k) becomes wobbly, just before, and especially after, the end-point. The accuracy and reproducibility are considerably reduced. They are about 2% for 5 mg of sulfate and somewhat more for 2 mg. The conclusion is that the cuvette is too large for such small amounts of sulfate. There is hardly any reason to doubt that the results would be more accurate in a smaller cuvette. After all, not the amount of sulfate, but its concentration, is the decisive factor.

INTERFERING IONS

It is well known that alkali salts are taken up by a barium sulfate precipitate with the formation of products such as $BaSO_4 \cdot X_2SO_4$; this would lead to a decreased consumption of the titrant and this was, in fact, confirmed in our titrations. The table below gives the consumption of $M/50$ aqueous barium nitrate for the titration of the usual titration mixture of 5 ml $M/50$ potassium sulfate, 5 ml water, 7 ml ethanol, and 7 ml *n*-butanol. To this mixture was added an equimolar amount of KCl, NaCl, LiCl, and NH_4Cl. The theoretical consumption was, of course, 5.00 ml.

250 mg KCl	4.73 ml
196 mg NaCl	4.76 ml
143 mg LiCl	4.75 ml
180 mg NH_4Cl	4.80 ml

Contrary to the finding of BOBTELSKY[1] (top of p. 187), to the effect that there was a remarkable difference in the behaviour of potassium and ammonium salts, we found the interference of equimolar amounts of the different alkali chlorides to be of about the same magnitude.

Unfortunately, the magnitude of the errors caused by the presence of alkali salts cannot be accurately predicted. With different amounts of potassium chloride added to the usual titration mixture we found:

750 mg KCl	— 4.40 ml	50 mg KCl	— 4.75 ml
250 ,, ,,	4.65 ,,	35 ,, ,,	4.72 ,,
250 ,, ,,	4.73 ,,	25 ,, ,,	4.92 ,,
100 ,, ,,	4.75 ,,	25 ,, ,,	4.90 ,,
50 ,, ,,	4.80 ,,	15 ,, ,,	4.84 ,,

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Evidently, there are elements of chance in the occlusion of alkali salts in the precipitate.

Since calcium sulfate in only very sparingly soluble in most alcohol–water mixtures, calcium ions are particularly bothersome if present in any appreciable amount. However, we found that this difficulty can be easily met by the addition, prior to the titration, of the required amount of ammonium oxalate. A large excess should be avoided because of the slight disturbance by ammonium salts, as noted above. The titration then starts from a turbid suspension of calcium oxalate which does not seriously hinder the sulfate titration. Of course, the galvanometer must now be slightly more sensitive than in the normal case.

Magnesium salts cause a slight, but nevertheless perceptible, lowering of the results. We found that here too the addition of small amounts of ammonium oxalate improved the results. This seems to confirm the heretofore doubtful assertion that magnesium ions form complexes with oxalate ions.

Small amounts of phosphate ions do not interfere at this pH of 1.5.

As is usual with the precipitation of barium sulfate, Fe^{+3} and Al^{+3} are the most troublesome of all, in that they give rise to very low results. Here again, as with calcium sulfate we found that at least part of the difficulties can be met by precipitating the interfering ions beforehand, now using the required amount of ammonium phosphate. As long as the amounts of iron and aluminium present are not greater than that of sulfate, reasonably exact results are obtained. The point of intersection of the titration curve is unsharp because of a rounding of the two branches. An extrapolation from the straight portions approximately produces the theoretical values.

SUMMARY

We found that a mixture of 2 parts water, 1 part ethanol, and 1 part *n*-butanol is the most suitable medium for the heterometric titration of small amounts of sulfate (2–20 mg). The addition of protective colloids is not necessary if the solution is stirred vigorously during the course of the titration. The disturbing effect of some other ions was investigated. Calcium, aluminium, and ferric iron can be precipitated beforehand in the cuvette without seriously hindering the sulfate titration.

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Received September 30th, 1957

A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF NICKEL

by

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INTRODUCTION

It has been found that the stable colored complex formed in a reaction of versene with nickel can be used as a spectrophotometric method for the determination of nickel. The spectra for the nickel versene complex show three absorption bands, one in the ultraviolet, one in the visible, and one in the near infrared region. The latter absorption band which shows a maximum at 1000 mμ, was chosen because many of the metal complexes of versene do not absorb at this wave length. It was possible to determine nickel in the presence of the following ions: aluminum(III), beryllium(II), calcium(II), cadmium(II), chromium(III), iron(III), mercury(II), manganese(II), lead(II), strontium(II), thorium(IV), and zinc(II). An ion exchange separation technique was employed to separate cobalt, copper, and large amounts of iron since they were found to interfere. Nitroso-R salt was employed as a masking agent for cobalt in nickel-cobalt mixtures. Results indicate that this method can be applied successfully to the determination of nickel in the presence of a large number of elements without interference.

Reagents

Versene solution - 74.5 g (0.2 moles) of disodium dihydrogen ethylenediaminetetraacetate dihydrate (reagent grade) obtained from the J. T. Baker Chemical Co. was dissolved in water and diluted to 1 l.

Nitroso-R salt solution - 20 g of practical grade nitroso-R salt (1-nitroso-2-naphthol-3,6-disulfonic acid, disodium salt) obtained from Eastman Organic Chemicals was dissolved in water and diluted to 1 l. The solution was stored in the dark.

Sodium acetate solution - 500 g of anhydrous sodium acetate was dissolved in 1 l of water.

Sodium hydroxide - Saturated solution.

Nitric acid - $8N$.

Hydrochloric acid - 8 and $12N$.

Standard nickel solutions - 0.400 and 1.800 g of spectroscopically pure nickel obtained from Johnson, Matthey and Co., London, were dissolved in dilute nitric acid and each diluted to exactly 1 l.

Apparatus

All quantitative measurements were made with a Beckman Model B spectrophotometer using matched 5.000-cm cylindrical corex cells. A Jones reductor (300 mm length and 20 mm diameter) was used to construct an ion exchange column. A 1-in. thick glass wool plug was used to support a 210-mm column of a strong base ion exchange resin, Amberlite IRA-400.

PROCEDURE

Determination of nickel

To the nickel solution which may contain the cations mentioned in Table I and which was concentrated to 5–10 ml in a 150-ml beaker, add 40 ml of $0.2M$ versene and 10 ml of sodium acetate solutions. Adjust to a pH of 4.0 with a saturated sodium hydroxide solution. Transfer the solution to

TABLE I

METALS WHICH MAY BE PRESENT WITHOUT INTERFERING IN THE DETERMINATION OF NICKEL

Concentration of nickel was 2 mg to 20 mg

Ion taken	*Maximum mg*	*No. runs*	*Average difference mg*
Al(III)	150	6	0.03
Be(II)	100	8	0.08
Ca(II)	100	7	0.05
Cd(II)	100	7	0.05
Cr(III)	100	8	0.07
Fe(III)	20	8	0.07
Hg(II)	100	6	0.05
Mn(II)	100	7	0.03
Pb(II)	100	8	0.03
Sr(II)	100	6	0.05
Th(IV)	125	8	0.04
Zn(II)	100	10	0.06

a 100-ml volumetric flask and dilute to the mark. With matched 5.000-cm cylindrical corex cells measure the absorbancy at 1000 mμ against a reference solution prepared in the same manner without nickel. The nickel concentration is interpreted from a calibration curve.

Determination of nickel after the removal of cobalt, copper and iron by ion exchange

To the nickel solution containing cobalt(II), copper(II) and large amounts of iron(III), which has been concentrated to 5–10 ml in a 150-ml beaker, add 20 ml of concentrated hydrochloric acid. Pass the solution through an ion exchange column of Amberlite IRA-400 resin which has been washed with 100 ml of distilled water followed by 50 ml of 8*N* hydrochloric acid. Operate the column at a flow rate of 4–5 ml/min and wash with 130 ml of 8*N* hydrochloric acid. Collect the sample and washings in a 250-ml beaker and concentrate to 10 ml. Prepare a reference solution by concentrating 160 ml of 8*N* hydrochloric acid to 5–10 ml. Measure the absorbancy of the solutions as described under the determination of nickel.

TABLE II

DETERMINATION OF NICKEL IN THE PRESENCE OF OTHER METALS

Ion mixture	*mg*	*Nickel taken mg*	*Nickel found mg*	*Difference mg*
Fe(III)	5	4.00	3.92	−0.08
Al(III)	25	18.10	18.14	0.04
Mn(II)	25			
Cd(II)	25	4.00	4.04	0.04
Ca(II)	25	18.10	18.18	0.08
Al(III)	25			
Sr(II)	25			
Fe(III)	5	4.00	4.08	0.08
Al(III)	50			
Al(III)	20	4.00	3.96	−0.04
Zn(II)	20			
Pb(II)	20			
Sr(II)	20			
Ca(II)	20			
Cd(II)	25	4.00	4.00	0.00
Al(III)	25	18.10	18.18	0.08
Mn(II)	50			

Average difference in mg of nickel = ± 0.06

Determination of nickel in nickel–cobalt mixtures

To the nickel solution containing cobalt which has been concentrated to 5–10 ml in a 150-ml beaker, add 10 ml of sodium acetate solution and 40 ml of nitroso-R salt solution. Adjust the pH of the solution to between 5 and 7 with sodium hydroxide to promote the formation of the cobalt complex. Allow to stand for 10 min. Heat the solution until it begins to boil and immediately add 10 ml of $8N$ nitric acid. Continue heating for 20 sec. Remove and cool rapidly to room temperature with stirring in an ice bath. Add 10 ml of $0.2M$ versene and adjust to a pH of 4.0 with saturated sodium hydroxide. Transfer the solution to a 100-ml volumetric flask and dilute to the mark. Measure the absorbancy at 1000 mμ against a reference solution prepared the same way without nickel and cobalt. The nickel concentration is interpretated from the calibration curve.

RESULTS AND DISCUSSION

Table I shows the maximum concentration of each ion, the number of determinations made and the average difference in mg of nickel per determination. Nickel was determined in the presence of various mixtures of these metals. The results with five mixtures are shown in Table II. These determinations showed an average difference of ± 0.06 mg. The presence of the following elements interfered: cerium(IV), bismuth(III), silver(I), barium(II), copper(II), cobalt(II), magnesium(II), and vanadium(IV).

TABLE III

DETERMINATION OF NICKEL AFTER AN ION EXCHANGE SEPARATION

Ion taken	*mg*	*Nickel taken*	*Nickel found mg*	*Difference mg*
Fe(III)	400	2.00	2.08	0.08
	500	18.10	18.06	−0.04
	600	4.00	3.96	−0.04
	700	18.10	18.10	0.00
	800	2.00	2.04	0.04
	900	18.10	18.18	0.08
Cu(II)	2.5	18.10	18.10	0.00
	3.0	4.00	3.96	−0.04
	5.0	2.00	2.04	0.04
	7.5	2.00	2.08	0.08
	7.5	18.10	18.18	0.08
Co(II)	10.0	18.10	18.02	−0.08
	15.0	2.00	1.96	−0.04
	17.5	4.00	3.96	−0.04
	20.0	18.10	18.14	0.04
	25.0	18.10	18.10	0.00
	27.5	2.00	2.04	0.04
	30.0	2.00	2.04	0.04
	30.0	18.10	18.10	0.00
Fe(III)	200	2.00	2.08	0.08
Co(II)	5	18.10	18.10	0.00
Cu(II)	2			
Co(II)	15	2.00	2.00	0.00
Cu(II)	2.5	18.10	18.22	0.12
Fe(III)	400	2.00	2.08	0.08
Cu(II)	2.5	18.10	18.10	0.00
Fe(III)	300	2.00	2.04	0.04
Co(II)	2.5			
Cu(II)	2			

Average difference in mg of nickel = ± 0.04

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As previously stated, the presence of cobalt, copper, and large amounts of iron interfere. KRAUS AND NELSON[1] have reported the distribution coefficients for the metal chloride complexes with a strong base ion exchange resin. Using this information, it was possible to separate cobalt, copper and iron from nickel. Nickel did not form a complex with the chloride ion and passed through the column, whereas cobalt, copper and iron formed a chloride complex and were absorbed in the presence of 8*N* hydrochloric acid. Table III shows some typical results obtained for nickel after an ion exchange separation from iron, cobalt and copper. The results of these determinations showed an average difference of ± 0.04 mg.

For nickel-cobalt mixtures nitroso-R salt was used as a masking agent for cobalt prior to the nickel determination, as has been discussed previously[2]. Nickel was determined in the presence of up to 12.5 mg of cobalt as shown in Table IV. These determinations showed an average difference of ± 0.06 mg. The presence of other elements gave erratic results and must be absent. This prodecure was tested by two students enrolled in undergraduate quantitative analysis. They obtained results within the limits described for this method. Up to 20.00 mg of nickel was determined with a maximum error of ± 0.10 mg.

TABLE IV

DETERMINATION OF NICKEL IN NICKEL-COBALT MIXTURES

Cobalt taken mg	*Nickel taken* mg	*Nickel found* mg	*Differences* mg
5.0	5.00	5.00	0.00
	11.58	11.50	−0.08
	16.16	16.10	−0.06
	17.25	17.28	0.03
10.0	5.00	5.12	0.12
	10.04	10.11	0.07
	11.58	11.50	−0.08
	15.04	15.02	−0.02
	17.25	17.33	0.08
12.5	2.01	2.04	0.03
	4.01	3.96	−0.05
	17.25	17.33	0.08
	17.25	17.36	0.11
	18.10	18.14	0.04

Average difference in mg of nickel = ± 0.06

ACKNOWLEDGEMENT

The authors wish to express their thanks to the American Cyanamid Company for support of this work in the form of a Research Fellowship awarded to L. D. B.

SUMMARY

A photometric method for the determination of nickel using versene is described. Up to 20 mg of nickel can be determined with a maximum deviation of ± 0.10 mg. The effect of interfering elements, concentrations, accuracy and limitations of the method are discussed.

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Received October 31st, 1957

ÉLECTROACTIVITÉ DES HALOGÉNURES

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Le comportement électrochimique des halogénures nous a conduit à faire l'hypothèse suivante. Sur une électrode de platine poli les ions simples I^-, Br^-, Cl^-, sont beaucoup moins électroactifs que les ions complexes correspondants, I_3^-, Br_3^- ou Br_2Cl^-. Nous apportons, dans l'étude suivante, différents arguments en faveur de cette hypothèse.

ELECTROACTIVITÉ DES IODURES

Le mécanisme de l'oxydation des iodures sur une électrode de platine poli peut être représenté soit par l'équation

$$2\,I^- - 2\,e \rightleftharpoons I_2 \qquad (1)$$

soit par les équations:

$$2\,I_3^- - 2\,e \rightleftharpoons 3\,I_2 \qquad (2)$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (3)$$

Dans l'un ou l'autre cas la vitesse d'oxydation des iodures est fonction de la concentration de l'iode moléculaire. Mais alors que d'après l'équilibre (1) cette oxydation est plus difficile en présence d'iode, d'après l'équilibre (3) la présence d'iode favorise la formation d'ions I_3^- qui sont seuls électroactifs (2). Pour trancher entre ces deux mécanismes il suffit d'étudier les déformations que subissent les courbes intensité-potentiel relatives à l'oxydation d'une solution d'iodure lorsque l'on fait varier la concentration de l'iode au voisinage de l'électrode. Certaines de ces courbes ont été étudiées par différents auteurs[1,2,9,10].

Nous rappelons ici quelques résultats de l'étude de KOLTHOFF ET JORDAN[2]. Ces auteurs ont tracé les courbes $i = f(E)$ (intensité-potentiel) dans les milieux suivants: acide perchlorique, tampon acétique, tampon phosphate. Ils ont admis que le système était rapide en milieu acide, mais devenait moins rapide en milieu tampon acétique. Enfin, en milieu phosphate, la courbe $i = f(E)$ présentait un maximum tandis qu'en milieu de soude la vague d'oxydation disparaissait complètement. Ces auteurs ont observé en outre qu'en présence d'ions Br^- ou Cl^-, le potentiel de demi-vague $E_{1/2}$ était déplacé vers les potentiels positifs, ce qui traduit une plus grande difficulté d'oxydation des iodures dans les milieux complexant l'iode (I_2Cl^-, I_2Br^-). Tous ces faits expérimentaux sont en faveur d'un mécanisme d'oxydation régi par les équations

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(2) et (3) qui traduisent le fait que les ions I^- sont moins électroactifs que les ions I_3^-.

Pour étayer cette hypothèse nous nous sommes proposés d'étudier la déformation des courbes $i = f(E)$ lorsque l'on fait varier la concentration de l'iode à l'électrode: adjonction d'iode, réduction immédiate de l'iode formé électrochimiquement ($S_2O_3^{-2}$), ou alcalinisation de la solution qui entraine la dismutation rapide de l'iode formé.

Influence de l'iode ajouté

D'après ce que nous venons de dire, une solution d'ions I^- deviendra plus électroactive après addition d'iode moléculaire. Par conséquent, à potentiel constant, l'intensité d'électrolyse d'une solution d'iodure doit croître par addition d'iode (à condition que le potentiel choisi soit suffisamment positif pour que la réduction de I_2 intervienne peu). Nous avons constaté expérimentalement une nette augmentation de l'intensité d'électrolyse par addition d'iode lorsque le potentiel est maintenu à la valeur E = 600 mV. Dans tout ce qui suit nous prendrons comme origine des potentiels celui d'une électrode au calomel saturée de chlorure de potassium.

Remarque. Nous avons opéré à pH 3, car en milieu acide l'oxydation des iodures par l'air est très rapide[3] et une addition ultérieure d'iode reste sans effet.

Influence du thiosulfate

Bien que réduisant l'iode, le thiosulfate est beaucoup moins électroactif que l'iodure, comme l'indique la Fig. 1.

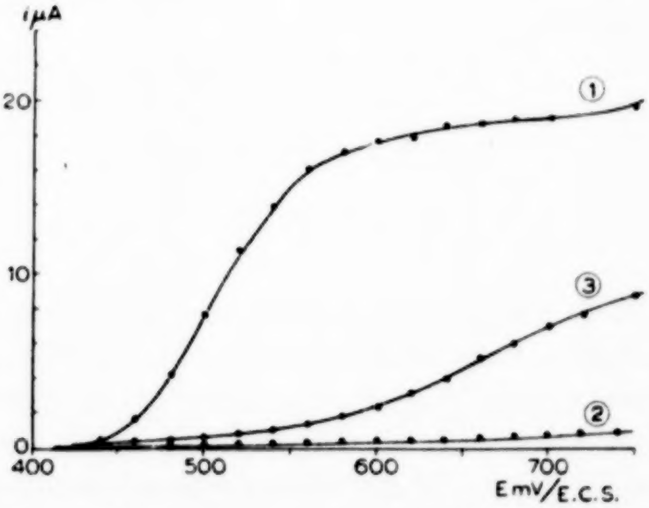

Fig. 1. Courbe 1 I^- $2 \cdot 10^{-4} M$, tampon monochloracétique M, pH 3.
2 $S_2O_3^{-2}$ $2 \cdot 10^{-3} M$, tampon monochloracétique M, pH 3.
3 I^- $2 \cdot 10^{-4} M$; $S_2O_3^{-2}$ $2 \cdot 10^{-3} M$, tampon monochloracétique M, pH 3.

Si on désire oxyder les iodures en présence de thiosulfate, il se produira la réaction chimique secondaire:

$$I_2 + 2\,S_2O_3^{-2} \rightleftharpoons S_4O_6^{-2} + 2\,I^- \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

Si le processus électrochimique était régi par l'équation (1) l'iodure régénéré selon l'équation (4) serait de nouveau oxydé et l'on aurait une vague catalytique[4]. Si le processus électrochimique est régi par les équations (2) et (3) (c'est-à-dire oxydation des ions I_3^-) l'équation (4) indique une consommation de l'iode donc une diminution de l'intensité d'électrolyse à un potentiel donné. Ce phénomène a été constaté expérimentalement et est représenté sur la Fig. 1. La courbe 3, qui représente l'oxydation des iodures à pH 3 en présence de thiosulfate, indique que l'électroactivité de la solution a presque disparu jusqu'à 750 mV puis augmente légèrement sans permettre d'atteindre le palier de diffusion représenté sur la courbe 1.

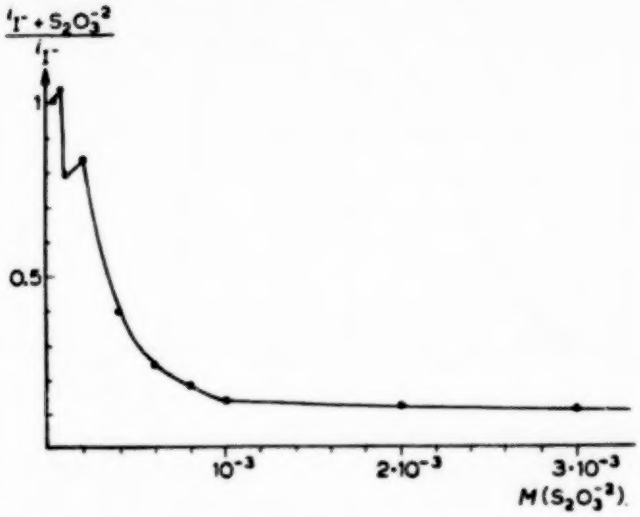

Fig. 2. Variation de l'intensité d'électrolyse pour $E = 500$ mV/E.C.S. en fonction de la concentration du thiosulfate présent.
$I^- = 5 \cdot 10^{-4} M$, pH 3; en abcisse: $M(S_2O_3^{-2})$; en ordonnée: intensité d'électrolyse en présence de thiosulfate/intensité d'électrolyse en l'absence de thiosulfate.

La Fig. 2 représente la variation de l'intensité de courant (pour $E = 500$ mV) lorsque l'on ajoute des quantités croissantes de thiosulfate. On voit que le thiosulfate agit comme inhibiteur de l'oxydation des iodures et que cette inhibition devient complète dès que la concentration du thiosulfate est telle que le rapport $\frac{S_2O_3^{-2}}{I^-} \geqslant 2$ dans les conditions indiquées.

Remarque. La diminution de l'électroactivité des iodures en présence de thiosulfate pourrait aussi être due à un empoisonnement de l'électrode de platine en présence de thiosulfate (adsorption). Cet empoisonnement existe d'ailleurs puisqu'une électrode de platine, polarisée anodiquement ($E \leqslant 750$ mV) dans une solution de thiosulfate, a un comportement différent qui se traduit par une légère diminution de l'électroactivité des iodures sur cette électrode. Cette diminution est cependant trop peu importante pour expliquer la disparition complète de l'électroactivité des iodures en présence de thiosulfate lorsque le potentiel demeure inférieur à 750 mV. De plus, un phénomène d'inhibition par adsorption ne devrait pas être spécifique des ions $S_2O_3^{-2}$; les ions SO_4^{-2}, très voisins, n'apportent aucune modification aux courbes de polarisation des iodures. Nous pensons donc que ce sont bien les propriétés réductrices du thiosulfate qui sont responsables des déformations observées sur les courbes de polarisation des iodures.

Influence du pH

D'après les équilibres suivants:

$$I_2 + OH^- \rightleftharpoons I^- + IOH \quad \text{et} \quad 3\,I_2 + 6\,OH^- \rightleftharpoons 5\,I^- + IO_3^- + 3\,H_2O$$

le pH doit avoir une influence sur la concentration des molécules d'iode[3]. Une augmentation du pH entraine une diminution de la concentration de l'iode moléculaire. D'après notre hypothèse cette augmentation provoquera une diminution de l'électroactivité d'une solution d'iodure. Sur la Fig. 3 sont représentées les courbes de polarisation relatives à l'oxydation des iodures à différents pH. L'augmentation du pH provoque d'une part un décalage du $E_{1/2}$ ($\triangle E \cong 45 \pm 5$ mV entre pH 0 et pH 3 par exemple),

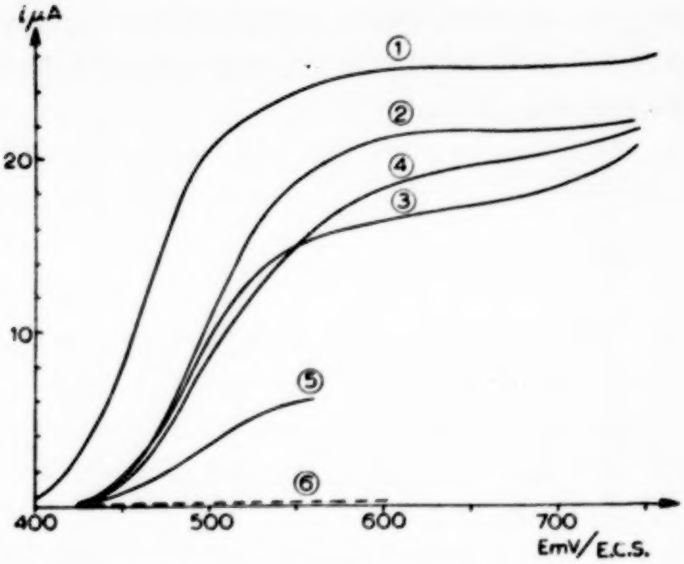

Fig. 3. Influence du pH. $I^- = 2\cdot10^{-4}M$.
(1) $HClO_4$ *N*; (2) pH 3; (3) pH 5; (4) pH 7; (5) pH 9; (6) NaOH *N*.

d'autre part une montée moins rapide de l'intensité du courant en fonction du potentiel (système plus lent) et enfin une diminution de la hauteur du palier de diffusion. Cette diminution s'accompagne d'ailleurs d'une décroissance de l'intensité en fonction du temps qui empêche tout tracé de la fin de la courbe pour des pH égaux ou supérieurs à 9. Nous notons comme KOLTHOFF ET JORDAN[2] l'ont déjà signalé, la disparition complète de la vague anodique des iodures en milieu de soude. Nous constatons aussi l'anomalie suivante: en tampon phosphorique (pH 7), la hauteur du palier de diffusion est supérieure à celle obtenue en tampon acétique.

Tous ces faits traduisent bien une diminution de l'électroactivité des iodures lorsque la concentration de l'iode à l'électrode diminue, c'est-à-dire quand le pH augmente.

Influence des ions Br^- et Cl^-

Le complexe I_2Cl^- étant peu stable (p*K* 0.3 à 0.5) il faut un grand excès d'ions Cl^- pour déformer la vague d'oxydation des iodures. D'aprés KOLTHOFF ET JORDAN[2], aucune déformation n'est observée en milieu HCl 0.1*N* il faut être en milieu Cl^- 1*M* pour observer effectivement un déplacement de la courbe vers les potentiels positifs. Le complexe I_2Br^- (p*K* 1.1 à 1.2) est plus stable et KOLTHOFF signale qu'en milieu HBr 0.1*N* le potentiel de demi-vague est égal à 0.65 V alors qu'en milieu $HClO_4$ 0.1*N* il est égal à 0.5 V.

Réalisation expérimentale

Nous avons constaté qu'une électrode de platine poli plongée dans une solution de $SnCl_2$ dans HCl 12*N* pendant 2 min, lavée à HCl, puis à l'eau distillée, fournissait ensuite des résultats reproductibles à condition de ne pas la porter à un potentiel supérieur à 0.75 V: Cette condition était compatible avec l'étude de l'oxydation des iodures dont la vague est située entre 0.4 V et 0.6 V.

La Fig. 4 représente la courbe de polarisation des iodures en milieu $HClO_4$ *N* lorsque le potentiel varie de 0.4 V à 0.75 V puis de 0.75 V à 0.4 V: les deux tracés sont superposés à 5 mV près. Si la polarisation est poussée jusqu'à 0.8 V la superposition disparaît, la surface de l'électrode de platine a été altérée, un nouveau traitement s'impose. Comme nous l'avons signalé, en présence de thiosulfate, il est nécessaire de traiter l'électrode pour chaque polarogramme.

Le mode de polarisation utilisé est analogue à celui exposé dans un précédent mémoire[5]: variation discontinue du potentiel de façon à pouvoir atteindre l'état de régime (lorsqu'il existe). Ici l'intensité de courant a été enregistrée à l'aide d'un suiveur de spot SEFRAM: le potentiel était toujours maintenu constant à l'aide d'un potentiostat.

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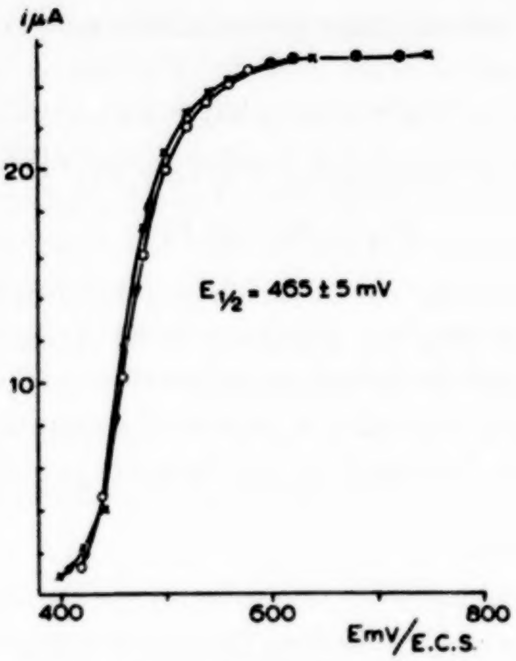

Fig. 4. I⁻ $2 \cdot 10^{-4}M$, $HClO_4$ N
× aller 400 mV → 750 mV.
o retour 750 mV → 400 mV.

La cellule utilisée est constituée par 3 électrodes: l'électrode indicatrice: fil de platine (l = 6 mm, r = 0.2 mm), l'électrode auxiliaire et l'électrode de référence, sont des électrodes au calomel saturé: elles sont reliées à la solution par des ponts d'agar-agar au nitrate de potassium.

ÉLECTROACTIVITÉ DES BROMURES

Utilisation des courbes de polarisation $i = f(E)$

Sur la Fig. 5 nous représentons la courbe d'oxydation du bromure ($5 \cdot 10^{-4}M$) en milieu $HClO_4$ N et la courbe de réduction du brome ($5 \cdot 10^{-4}M$) dans ce même milieu (aucune précaution n'a été prise pour éviter le dégagement du brome). La position respective de ces deux courbes nous montre qu'il s'agit d'un système lent, les potentiels de demi-vague anodique et cathodique étant distincts[6].

Le fait que la vague d'oxydation des bromures s'étende sur plus de 200 mV indique également qu'il s'agit d'une réaction électrochimique lente.

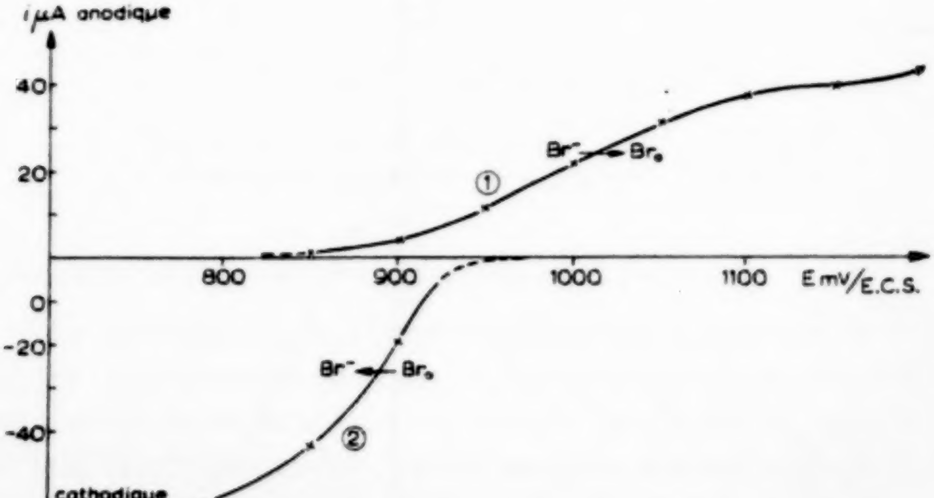

Fig. 5. Courbe (1) Br⁻ $5 \cdot 10^{-4}M$, $HClO_4$ N.
Courbe (2) Br_2 $5 \cdot 10^{-4}M$, $HClO_4$ N.

Comme dans le cas des iodures nous avons admis que la réaction électrochimique prédominante était

$$2\,Br_3^- \rightleftharpoons 3\,Br_2 + 2\,e \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

cette réaction est précédée par la formation des ions Br_3^- selon

$$Br_2 + Br^- \rightleftharpoons Br_3^- \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

Toute réaction susceptible d'agir sur la formation des ions Br_3^- perturbera la courbe de polarisation: addition de Br_2, pH, addition de Cl^- complexant Br_2. Plutôt que de tracer la totalité de la courbe de polarisation, nous avons préféré, pour des questions de reproductibilité (*cf.* p. 49) travailler à potentiel constant et observer la variation de l'intensité de l'électrolyse lorsque l'un des facteurs précédents varie.

Addition de brome moléculaire

L'addition de brome moléculaire à une solution de bromure provoque une augmentation de l'électroactivité de cette solution. Nous avons mis ce phénomène en évidence de la façon suivante:
A un potentiel où le brome moléculaire n'est ni réduit, ni oxydé (950 mV) l'intensité du courant résiduel ne sera pas influencée par l'addition de brome moléculaire. Au même potentiel les ions Br^- sont électroactifs et nous avons constaté que l'addition de brome moléculaire provoque une augmentation de l'intensité d'électrolyse. Cette expérience est illustrée par la Fig. 6.

Influence du pH. Mode de tracé

Le tracé des courbes de polarisation relatives à l'oxydation des bromures offre un certain nombre de difficultés: quel que soit le pH, la zone de potentiel où est située cette courbe (850 mV à 1,300 mV), Fig. 5 implique que l'électrode de platine soit portée à des potentiels où sa surface est altérée (oxydation anodique[7]). Il faut donc traiter l'électrode entre le tracé de chaque courbe et la reproductibilité des mesures est beaucoup moins bonne que dans le cas des iodures: de plus, dès que le pH est égal ou supérieur à 2, l'intensité de courant devient instable et les courbes tracées

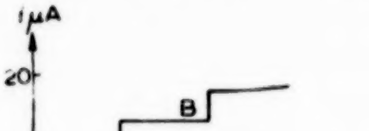

Fig. 6. E = 950 mV/E.C.S.; en A : addition de Br^- (entre A et B Br^- $5\cdot10^{-4}M$); en B : addition de Br_2.

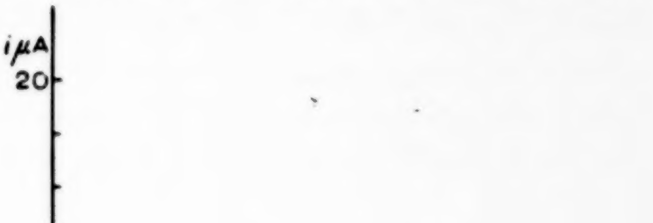

Fig. 7. E = 950 mV/E.C.S. Br^- $5\cdot10^{-4}M$. Influence du pH sur l'intensité d'électrolyse.

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ne sont plus reproductibles. Pour étudier l'influence du pH nous avons préféré opérer à potentiel constant, ici $E = 950$ mV, et faire varier brusquement le pH par addition d'un petit volume de soude concentrée (ce qui entraîne une dilution négligeable). Nous obtenons ainsi les points correspondant à pH 0, 1 et 2. Pour pH 3, nous ajoutons à la solution d'acide perchlorique N de l'acide monochloracétique ($N/10$) de façon à obtenir en neutralisant par la soude une solution tamponnée. Aux pH plus élevés, l'intensité de courant, constamment décroissante, atteint en 2 ou 3 min une valeur très voisine de celle de l'intensité résiduelle. La Fig. 7 résume l'influence du pH. Comme dans le cas des iodures, nous pensons que la dismutation du brome selon la réaction:

$$3\,Br_2 + 6\,OH^- \rightleftharpoons BrO_3^- + 5\,Br^- + 3\,H_2O$$

est responsable de cette diminution d'électroactivité.

Influence des chlorures

Comme précédemment, nous avons opéré à potentiel constant $E = 950$ mV et étudié la variation de l'intensité d'électrolyse d'une solution de bromure en fonction de la concentration des chlorures. La Fig. 8 illustre cette étude et met en évidence la disparition, par formation de complexes avec les chlorures, du brome produit électrochimiquement.

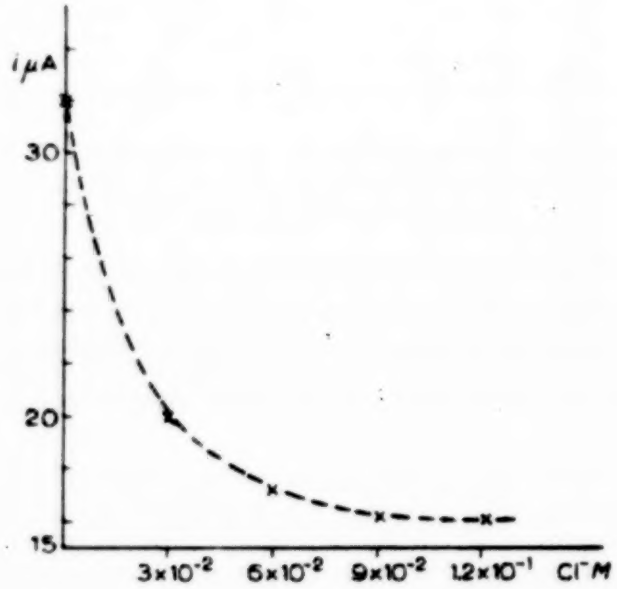

Fig. 8. $E = 950$ mV/E.C.S. Br^- $10^{-3}M$, $HClO_4$ N. Influence des chlorures sur l'intensité d'électrolyse.

Stabilité et reproductibilité des mesures. Traitement de l'électrode

En milieu acide les intensités de courant sont stables jusque vers 1150 mV. Au delà, l'intensité décroît constamment en fonction du temps. Comme nous l'avons dit, après le tracé d'une courbe de polarisation, la surface de platine est altérée et la courbe tracée sur une telle électrode oxydée électrochimiquement est toujours située au dessus de la première. Le traitement par le chlorure stanneux et l'acide chlorhydrique $12N$ déjà mentionné, nous a donné les meilleurs résultats (supérieurs en particulier au traitement par HNO_3 concentré). Dans ces conditions, nous obtenons une reproductibilité de 20 mV environ. Le montage est analogue à celui utilisé dans l'étude des iodures.

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Étude coulométrique

Oxydation electrochimique des bromures à potentiel contrôlé. Nous avons enregistré les courbes traduisant les variations de l'intensité d'électrolyse en fonction du temps à deux potentiels différents, au cours de l'oxydation des bromures sur une électrode de platine. Pour un potentiel $E = 890$ mV, la décroissance de l'intensité de courant en fonction du temps n'est pas logarithmique, comme le veut la théorie[8] (Fig. 9, courbe 1).

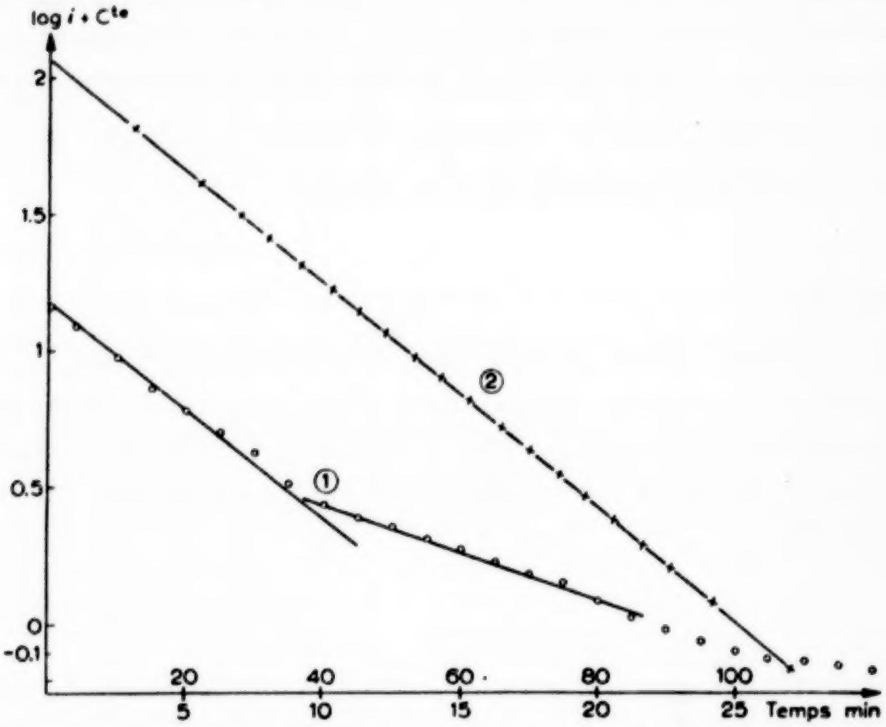

Fig. 9. Courbe (1) + Br^- $10^{-3}M$, $HClO_4$ N, $E = 890$ mV/E.C.S., 1 div. = 20 min.
Courbe (2) o Br^- $10^{-4}M$, $HClO_4$ N, $E = 1130$ mV/E.C.S., 1 div. = 5 min.

Il est probable que le brome formé, déplaçant les courbes de polarisation, est responsable de cette anomalie. Sur le palier de diffusion ($E = 1{,}130$ mV), cette décroissance est logarithmique comme l'indique la courbe 2 de la Fig. 9. C'est donc à ce potentiel que nous avons cherché à vérifier la proportionnalité entre la surface S délimitée par la courbe

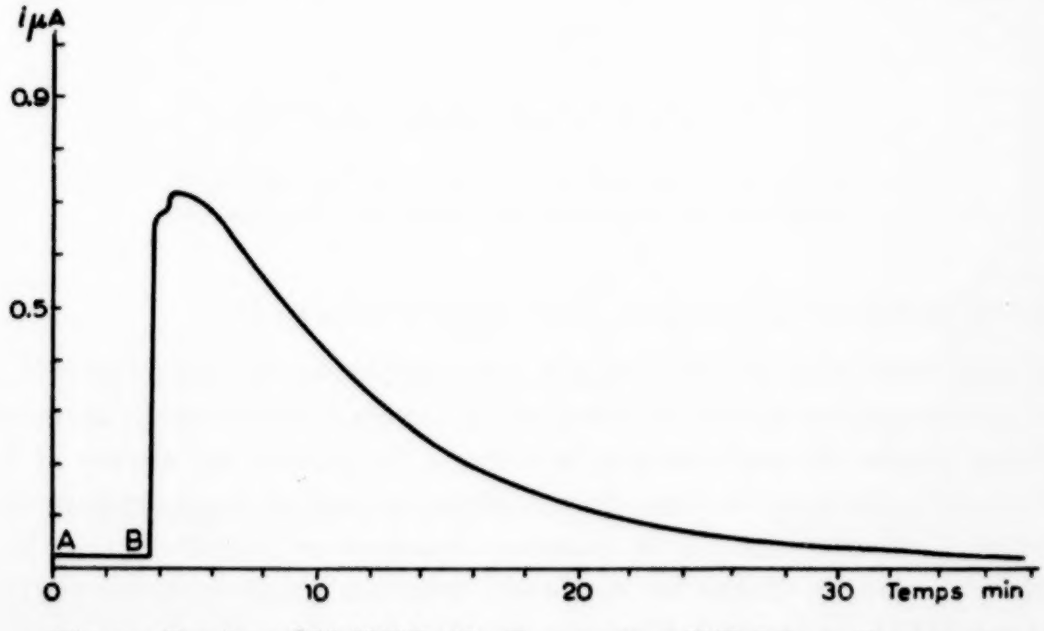

Fig. 10. Br^- $8 \cdot 10^{-5}M$, $HClO_4$ N. $E = 1{,}130$ mV/E.C.S. A B courant résiduel. En B addition de bromure.

$i = f(tps)$ (Fig. 10) et la concentration c du bromure en solution. La courbe (1) $S = f(c)$ de la Fig. 11 indique bien, sauf à l'origine, une relation linéaire entre la surface S et la concentration c du bromure. L'ordonnée à l'origine de cette droite devrait correspondre à la présence du courant résiduel; or le produit du temps d'électrolyse par l'intensité résiduelle déterminée avant l'addition de bromure dans la solution, est bien inférieure à cette ordonnée à l'origine. Il faut donc admettre que la valeur du courant résiduel est augmentée lorsque se produit une oxydation.

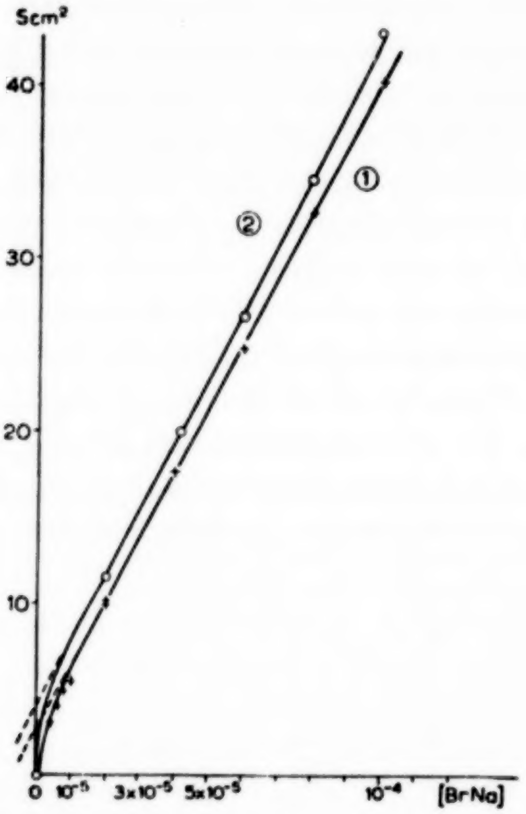

Fig. 11. Courbe (1) Br^- seul + $HClO_4$ N.
Courbe (2) Br^- en présence de Cl^- $8 \cdot 10^{-4} M$ + $HClO_4$ N.
S = surface de la courbe $i = f(t)$ pour E = 1,130 mV/E.C.S.
1 cm² = $1.3 \cdot 10^{-2}$ coulomb.

Réalisation expérimentale

Le potentiel est stabilisé par l'emploi d'un potentiostat[5]. L'intensité d'électrolyse est enregistrée en fonction du temps à l'aide d'un suiveur de spot (SEFRAM). Le galvanomètre employé est antivibratoire. L'anode de platine est un cylindre grillagé de 4 cm de haut et de 3 cm de diamètre.

L'électrode auxiliaire (cathode) est constituée d'un fil de platine plongeant dans une solution acide, concentrée de permanganate: la force contre-électromotrice de la pile est ainsi considérablement réduite, ce qui permet au potentiostat de fournir des intensités de courant plus élevées. Les compartiments anodique et cathodique sont séparés par un pont d'agar-agar au nitrate de potassium.

L'électrode de référence, au calomel saturé, est reliée également par un pont d'agar-agar à la cellule.

Le volume de solution utilisé est de l'ordre de 30 ml, le rapport surface/volume est ainsi augmenté le plus possible.

La cellule est remplie par l'électrolyte indifférent ($HClO_4$ N) qui est électrolysé pendant 5 à 10 min jusqu'à ce que l'on obtienne un courant résiduel constant. On ajoute alors un volume connu de bromure.

L'aire des courbes $i = f(t)$ est planimétrée, l'erreur absolue est de l'ordre de 1 cm².

En conclusion, nous pouvons dire que l'oxydation des bromures est lente et que le processus électrochimique à l'électrode est le suivant:

$$2\ Br_3^- - 2\ e \rightleftharpoons 3\ Br_2$$

Le brome produit électrochimiquement est utilisé par les ions Br^- présents dans la solution pour former l'ion complexe Br_3^- électroactif.

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Les courbes de polarisation relatives à l'oxydation des bromures sont affectées par la présence de brome libre (facilitant la formation de Br_3^-), par l'élévation du pH (provoquant la dismutation du brome) et par la présence de chlorure complexant le brome formé à l'électrode.

ÉLECTROACTIVITÉ DES CHLORURES

Dans un précédent mémoire[9], nous avions étudié le comportement électrochimique des chlorures à différentes concentrations en milieu acide normal: nous observions une diminution nette de l'électroactivité des chlorures avec la dilution. Ce phénomène pourrait s'expliquer en admettant qu'en milieu concentré il y a formation d'ions complexes Cl_3^- plus électroactifs que les ions simples; par dilution on provoque la dismutation du chlore à l'électrode. L'existence de complexes Br_2Cl^- étant connue, nous avons cherché à savoir si ces complexes étaient, eux aussi, plus électroactifs que l'ion simple.

En utilisant un dispositif d'enregistrement de courbes de polarisation, nous avons travaillé, comme dans le cas de bromures, à potentiel constant. Nous avons recherché le potentiel le plus positif où ni le brome $(5 \cdot 10^{-4} M)$ ni les ions Cl^- $(1.2 \cdot 10^{-2} M)$ ne sont oxydés de façon appréciable soit 1,000 mV. L'intensité du courant résiduel sera donc peu perturbée par l'adjonction de l'un ou l'autre de ces réactifs, mais la présence simultanée de brome et d'ions Cl^- provoquera une augmentation appréciable de cette intensité. D'après la Fig. 12, cette augmentation est plus importante lorsqu'on ajoute le brome aux chlorures que lorsque les réactifs sont ajoutés en sens inverse. Nous ne pouvons pas expliquer cette différence de comportement.

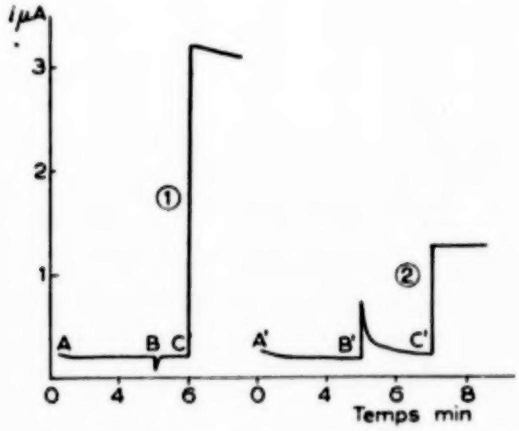

Fig. 12. Electroactivité du complexe Br_2Cl^-. $E = 1000$ mV/E.C.S. $HClO_4$ N. Courbe (1) A B courant résiduel. En B addition de Br_2; en C addition de HCl 12N. Courbe (2) A′ B′ courant résiduel. En B′ addition de HCl 12N; en C′ addition de Br_2.

Une étude coulométrique nous a permis de recouper ces résultats. L'oxydation du bromure à potentiel contrôlé peut être suivie par l'enregistrement de l'intensité d'électrolyse en fonction du temps. La surface délimitée par ces courbes, correspondant à la quantité d'électricité consommée, est proportionnelle à la concentration initiale de bromure.

Par ailleurs cette oxydation produit une quantité importante de brome. Les chlorures (non électroactifs en l'absence de brome) le deviendront au fur et à mesure de la formation du brome. Comparons les droites S (surface) $= f$ ((c) concentration du Br^-) relatives à des solutions de bromure contenant ou non des ions Cl^- (Fig. 11); nous constatons qu'en présence de chlorure la quantité d'électricité consommée est toujours plus élevée bien que les intensités du courant résiduel en présence et en l'absence de chlorure soient identiques au potentiel utilisé (1,130 mV). Ceci traduit bien une oxydation des chlorures en présence du brome formé électrochimiquement.

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Remarque. D'après les positions relativement distinctes des courbes de polarisation des bromures et des chlorures, l'oxydation sélective de bromure en présence de chlorure à potentiel contrôlé semblait facile à réaliser. Mais la formation d'ions Br_2Cl^- électroactifs rend un dosage coulométrique de cet ordre irréalisable.

Les trois halogénures semblent donc avoir un comportement électrochimique correspondant à une réaction du type $2\ X_3^- - 2\,e \rightleftharpoons 3\ X_2$. Toute réaction chimique rapide qui consomme l'halogène tend à diminuer l'électroactivité des halogénures (formation de complexe, dismutation, ou réduction de l'halogène). La présence initiale de l'halogène augmente par contre cette électroactivité.

RÉSUMÉ

Les courbes intensité–potentiel relatives à l'oxydation des iodures, bromures et chlorures sur une électrode de platine poli, subissent des déformations lorsque l'on fait varier les facteurs suivants: concentration initiale de l'halogène, pH, addition d'ions complexant ou réduisant l'halogène formé. L'analyse de ces déformations nous a conduit à admettre que les trois halogénures avaient un comportement électrochimique pouvant être représenté par une réaction du type:

$$2\ X_3^- - 2\,e \rightleftharpoons 3\ X_2$$

et non pas du type:

$$2\ X^- - 2\,e \rightleftharpoons X_2$$

Pour les bromures et les chlorures, l'étude coulométrique est en accord avec cette hypothèse.

SUMMARY

The intensity–potential curves pertaining to the oxidation of iodides, bromides and chlorides at a polished platinum electrode, undergo deformations when the following factors are varied: initial concentration of halogen, pH, addition of ions that complex or reduce the halogen formed. Analysis of these deformations has led us to assume that the electrochemical behaviour of the three halides can be represented by a reaction of the type:

$$2\ X_3^- - 2e \rightleftharpoons 3\ X_2$$

and not of the type:

$$2\ X^- - 2e \rightleftharpoons X_2$$

As far as bromides and chlorides are concerned, the coulometric study agrees with this hypothesis.

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Reçu le 1er novembre 1957

THE POLAROGRAPHIC DETERMINATION OF ALUMINIUM*

III. A PRELIMINARY STUDY OF THE MECHANISM OF THE ALUMINIUM-SOLOCHROME VIOLET R.S. REACTION

by

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INTRODUCTION

In Part I of this series[1] the polarography of aluminium was discussed in general and a study was made of the applicability of the method of WILLARD AND DEAN[2] which involves the modification, by aluminium, of the polarographic step due to the reduction of the azo dye solochrome violet R.S. In Part II[3] the development of a method for the determination of microgram amounts of aluminium in beryllium, based on the foregoing method, was described.

In the previous work, no study was made of the mechanism of the aluminium-dye reaction and of the molecular species formed. The work described here was therefore undertaken to provide information of this nature. In particular, a study has been made over a wider pH range than that hitherto investigated and determinations of the number of electrons transferred per molecule reduced at the electrode have been carried out by several methods. The ratio of dye to aluminium under various conditions of pH has also been determined.

EXPERIMENTAL

Unless otherwise stated, all polarography has been carried out on a Cambridge direct writing polarograph at 25° and *versus* the mercury pool anode. All potentials are quoted on the European sign convention. On this convention the potential of the saturated calomel electrode (S.C.E.) has been taken as +0.246 V *versus* the normal hydrogen electrode (N.H.E.).

The effect of pH on the aluminium-solochrome violet R.S. reaction

Aliquots equivalent to 125 μg of aluminium were placed in a series of 50-ml beakers, 20 ml of 0.05% solochrome violet R.S. solution and 4 ml of 2.5N ammonium acetate solution were added, followed by 5N perchloric acid and 10% sodium hydroxide in amounts necessary to give the desired pH, within the range 2 to 10. Each solution was then transferred to a 50-ml graduated flask and made up to volume with water. The flasks were heated at about 70° in a water bath for 10 min and, after cooling, aliquots were deoxygenated and polarographed. The pH of each solution was accurately determined on the remainder in the flask.

The results, given in Table I, showed that the height of the aluminium-dye step increased with increase in pH value until a steady state was reached in the pH range 4.2 to 5.0. This agreed with the findings of WILLARD AND DEAN[2] and corresponded to the pH used for the work already described[1,3]. At higher pH values the step height again increased until a second steady state occurred within the range pH 5.75 to 7.0. Instability was encountered when the pH was increased further. A graph of diffusion

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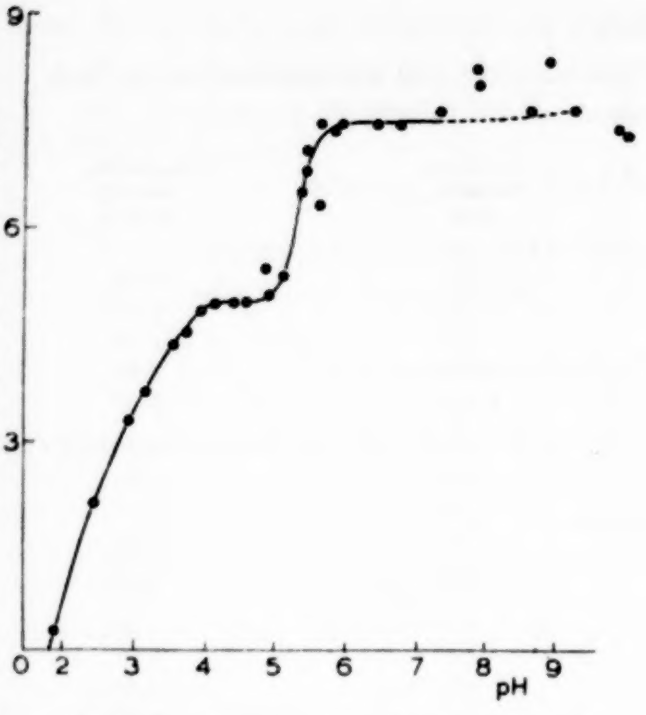

Fig. 1. Diffusion current constant *versus* pH. Solochrome violet R.S. (0.02%) in presence of 2.5 μg/ml aluminium.

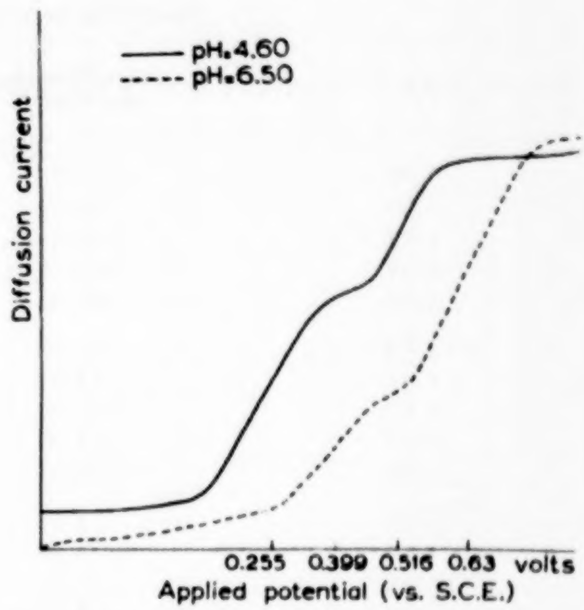

Fig. 2. Solochrome violet R.S. (0.02%) in presence of aluminium (2.5 μg/ml).

current constant *versus* pH is shown in Fig. 1 and typical polarograms at pH 4.6 and pH 6.5 are reproduced in Fig. 2. Conversion of the measured limiting diffusion currents to diffusion current constants has been made in order to render them independent of variable factors. This has been done by multiplying each diffusion current value by $\frac{1}{c\cdot m^{2/3}\cdot t^{1/6}}$ (in this case = 0.263), where c is the concentration in mmoles/l, m is the rate of flow of mercury in mg/sec and t is the drop time in sec.

Determination of the number of electrons transferred on reduction

Determination of the number of electrons transferred per molecule reduced (n) was made for the dye alone and in the presence of aluminium at pH 4.6. From these results the diffusion coefficients of the free dye and of the complex were calculated. For this work the "arithmetic average" method described by REYNOLDS AND SHALGOSKY[4] was employed. The microcell designed by these authors was used to contain the solution for polarography.

Solochrome violet R.S. at pH 4.6. A solution of solochrome violet R.S., containing 200 μg of dye per ml and buffered at pH 4.6, with an ammonium acetate–perchloric acid mixture was prepared. A portion of this solution was transferred to the polarographic cell and polarographed *versus* the mercury pool anode. 0.30 ml of this solution was then transferred to the microcell and electrolysed at the dropping mercury cathode for 20 min with the polarograph set to apply a steady potential difference of 0.9 V between the electrodes, using the mercury pool as anode. At the end of this period, hydrogen was bubbled through the solution for a few seconds by means of a fine glass capillary and a polarogram was then recorded.

This electrolysis and polarography was repeated several times. The results are given in Table II, below. A similar determination was made using the silver–silver chloride electrode as suggested by REYNOLDS AND SHALGOSKY[4]. The results were much less satisfactory.

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TABLE I

ALUMINIUM, 2.5 μg/ml (0.0296 mmoles/l) IN THE PRESENCE OF SOLOCHROME VIOLET R.S

Dropping mercury electrode $m^{2/3} t^{1/6} = 2.834$

pH	*Aluminium–dye step height*[a]	*Diffusion current* (i_d) (μA)	*Diffusion current constant*
1.95	1.0	0.052	0.20
2.50	10.5	0.546	2.06
3.03	16.5	0.858	3.24
3.24	18.5	0.962	3.64
3.60	22.0	1.145	4.32
3.83	23.0	1.188	4.52
4.02	24.5	1.275	4.81
4.20	25.0	1.301	4.92
4.50	25.0	1.301	4.92
4.60	25.0	1.301	4.92
4.89	27.5	1.430	5.40
4.96	25.5	1.328	5.01
5.13	27.0	1.405	5.30
5.25	28.5	1.482	5.60
5.42	33.0	1.718	6.48
5.50	34.5	1.795	6.78
5.54	36.0	1.871	7.07
5.68	32.0	1.665	6.29
5.74	38.0	1.978	7.46
5.92	37.5	1.950	7.36
6.02	38.0	1.978	7.46
6.50	38.0	1.978	7.46
6.84	38.0	1.978	7.46
7.40	39.0	2.014	7.66
7.94	42.0	2.182	8.25
8.60	43.5	2.261	8.55
8.74	39.0	2.014	7.66
9.03	42.5	2.210	8.35
9.40	39.0	2.014	7.66
10.00	37.5	1.950	7.36
10.08	34.5	1.795	6.78

[a] The step height values in this column were recorded at a sensitivity setting of $^1/_{20}$ on the Cambridge direct writing polarograph employed.

TABLE II

Number	*Time* (*sec*)	*Step height*[a] (*arbitrary units*)	*log* (*step height*)
1	0	44	1.6435
2	1200	41	1.6128
3	2400	37.5	1.5740
4	3600	35.0	1.5441
5	4800	31.5	1.4883

[a] See note in Table I.

The five results were paired in all ten possible ways and the number of electrons transferred was calculated from the formula:

$$n = \frac{M}{F} \cdot t \cdot \frac{i.av}{w}$$

Where M = Molecular weight of the dye (366.3)
F = the Faraday (96,500 coulombs)
t = time of electrolysis in seconds
$i_{av} = \dfrac{i_o + i_t}{2}$ where i_o and i_t are the limiting diffusion currents flowing at the beginning and end of the electrolysis.
w = weight of dye reduced.
$\left(\dfrac{i_o - i_t}{i_o}\ 0.3 \text{ concentration of dye}\right)$

The values obtained are listed in Table III.

TABLE III

Pairing of results	*Time interval (t sec)*	*W (µg)*	i_{av} *(µa)*	*Electrons transferred (n)*
1 and 2	1200	4.1	2.17	2.41
1 and 2	2400	8.86	2.08	2.14
1 and 3	3600	12.28	2.01	2.24
1 and 5	4800	17.1	1.92	2.05
2 and 3	1200	4.77	2.00	1.91
2 and 4	2400	8.22	1.94	2.16
2 and 5	3600	12.95	1.845	1.95
3 and 4	1200	3.41	1.845	2.47
3 and 5	2400	8.18	1.76	1.96
4 and 5	1200	4.87	1.76	1.82

The arithmetic mean of the above values for the number of electrons transferred gives:

$$n = 2.11. \text{ (Standard deviation } \sigma = 0.213)$$

The figures in Table II were also interpreted by the method of GILBERT AND RIDEAL[5] to provide an alternative result. In accordance with this method the log height is plotted *versus* time in seconds and the best straight line is drawn through the points. The value of n was then calculated from the expression for the slope of the graph which is

$$\text{Slope} \cdot n = \frac{-K_2}{K_1} \cdot \frac{0.4343}{F \cdot V}$$

Where K_1 = Concentration of reducible material in moles/l which would give a step height of 1 division.
K_2 = Diffusion current in equivalent to a step height of 1 division.
V = Volume of solution in litres.

The value obtained from the graph (shown in Fig. 3) was

$$n = 1.94$$

It was noted on examination of the polarograms obtained after electrolysis that a small step had appeared at —0.17 V. The height of this step, which is shown on the polarogram in Fig. 4, was approximately equal to the decrease in the step height of the dye caused by electrolysis. No further examination of this wave was made, but its probable nature is discussed later.

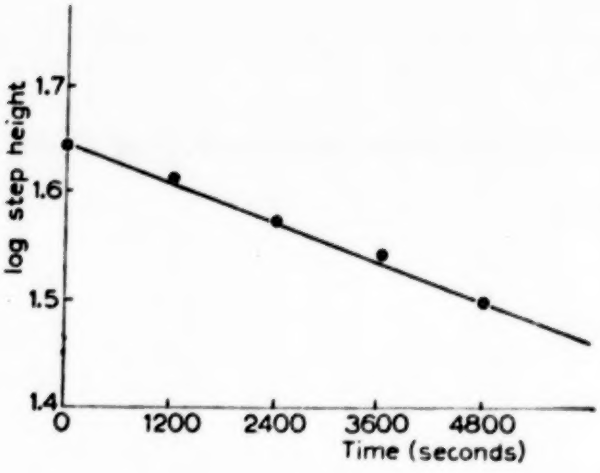

Fig. 3. Log step height *versus* time of electrolysis. Solochrome violet R.S. (200 μg/ml) at pH 4.60.

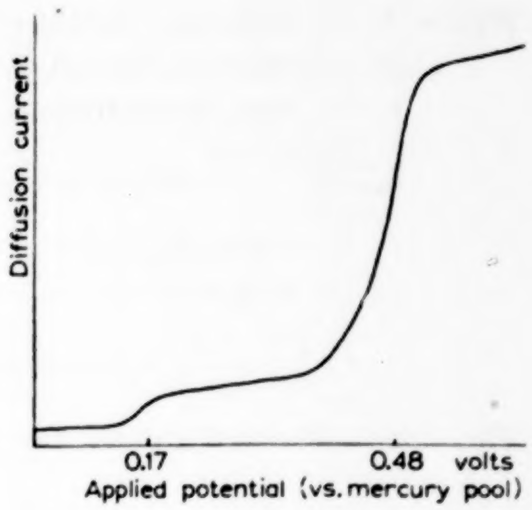

Fig. 4. Solochrome violet R.S. (200 μg/ml) after prolonged electrolysis at the dropping mercury cathode (pH 4.60).

Aluminium - solochrome violet R.S. at pH 4.6. 25 ml of a solution containing 200 μg aluminium and 0.005 g of solochrome violet R.S. buffered at pH 4.6 was prepared as before. The electrolysis was carried out as described above, except that the silver–silver chloride electrode was substituted for the mercury pool anode. The concentration of aluminium employed was chosen to give sufficient excess to eliminate the step due to free dye.

Table IV gives the results obtained; the values calculated for n together with the data for the calculation are listed in Table V. The irregular time intervals shown are caused by the addition to the time of electrolysis of the actual time of flow of the limiting diffusion current during the recording of the polarogram.

TABLE IV

Number	*Time (sec)*	*Step height (arbitrary units)*	*log (step height)*
1	0	49.0	1.6902
2	1321	45.0	1.6532
3	2642	41.5	1.6180
4	3963	38.5	1.5855
5	5284	34.5	1.5378
6	6605	31.0	1.4914

The average of the values for n in Table V gives

$$n = 3.81.$$

The results in Table IV were also interpreted by the method of GILBERT AND RIDEAL[5]. The graph used for this has not been included in view of its similarity to Fig. 3. The value obtained was

$$n = 4.11.$$

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TABLE V

Pairing of results	*Time interval (t sec)*	*W (μg)*	i_{av} *(μa)*	*Electrons transferred (n)*
1 and 2	1321	0.1675	1.86	3.98
1 and 3	2642	0.314	1.735	4.08
1 and 4	3963	0.44	1.675	4.23
1 and 5	5284	0.606	1.60	3.89
1 and 6	6605	0.753	1.533	3.76
2 and 3	1321	0.1465	1.66	4.19
2 and 4	2642	0.272	1.60	4.34
2 and 5	3963	0.439	1.515	3.82
2 and 6	5284	0.586	1.455	3.67
3 and 4	1321	0.1255	1.53	4.50
3 and 5	2642	0.293	1.455	3.68
3 and 6	3963	0.439	1.385	3.50
4 and 5	1321	0.1675	1.40	3.1
4 and 6	2642	0.314	1.36	3.21
5 and 6	1321	0.146	1.255	3.18

Calculation of diffusion coefficients

The values obtained above for *n*, the number of electrons transferred per molecule reduced, were employed to calculate the diffusion coefficients for the free dye and for the aluminium–dye species existing at pH 4.6. The calculation was made in each case by substitution in the Ilkovic equation. This gave the following diffusion coefficients:

$$D.\ (\text{dye at pH } 4.6) = 0.48 \cdot 10^{-5}\ \text{cm}^2\text{sec}^{-1}$$

$$D.\ (\text{dye–aluminium at pH } 4.6) = 0.44 \cdot 10^{-5}\ \text{cm}^2\text{sec}^{-1}.$$

Determination of the combining ratio of aluminium and solochrome violet R.S.

Ratio of aluminium and solochrome violet R.S. at pH 4.6. This determination was carried out by the method of JOB[6]. Equimolar solutions ($10^{-3}M$) of both solochrome violet R.S. and aluminium were prepared and total combined volumes of these solutions having volume ratios varying from 9:1 to 1:9 were added to a series of 25-ml graduated flasks. Addition of ammonium acetate and adjustment of pH to 4.6 with sodium hydroxide and perchloric acid were made as usual and, after heating in a water bath at 70° for 10 min, the flasks were cooled and an aliquot from each deoxygenated and polarographed. The details of solutions employed and the results obtained are given in Table VI.

The heights of the dye-aluminium steps were plotted *versus* the dye : aluminium ratios to give the curve shown in Fig. 5. The intersection of the straight portions of the graph (produced) occurred at a point equivalent to an aluminium : dye ratio of 3.15:6.83. This represents a ratio of 1:2.17 and the ratio of aluminium to dye in the species existing at pH 4.6 was therefore taken to be 1:2.

Ratio of aluminium and solochrome violet R.S. at pH 6.5. A further series of solutions was prepared exactly as described above except that the final pH was adjusted to 6.5. In view of the rather poor separation of steps at this *pH* it was decided to carry out the polarography by means of the linear-sweep cathode ray polarograph[7,8] since this instrument affords better resolution of steps.

The results obtained are given in Table VII and the graph of step height against aluminium : dye ratio is shown in Fig. 6.

TABLE VI

Vol. of $10^{-3}M$ *dye solution added (ml)*	*Vol. of* $10^{-3}M$ *aluminium solution added (ml)*	*Step height*[a] *(dye)*	*Step height*[a] *(dye–aluminium)*
10	0	77.0	—
9	1	49.5	16.0
8	2	24.5	32.5
7.5	2.5	13.5	39.5
7	3	6.5	43.5
6.5	3.5	2.5	45.0
6	4	1.5	43.0
5	5	1.0	36.5
4	6	—	29.0
3	7	—	21.5
2	8	—	14.5
1	9	—	7.0

[a] The step heights were obtained on the Cambridge direct writing polarograph with the sensitivity control set to $^1/_7$. The half-wave potentials of the steps were −0.45 V and −0.65 V *versus* the mercury pool for the free solochrome violet R.S. and for the dye–aluminium steps respectively.

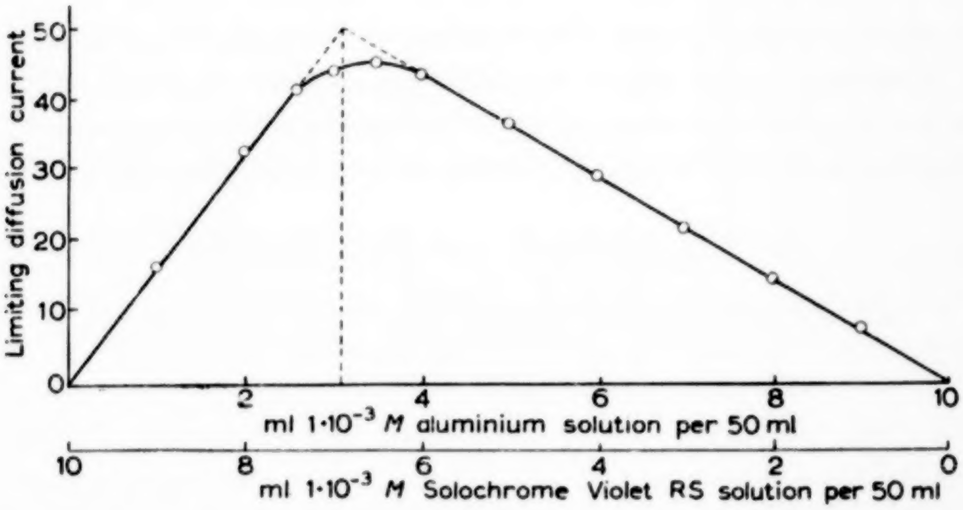

Fig. 5. Determination of the aluminium–solochrome violet R.S. ratio at pH 4.6. (JOB's method).

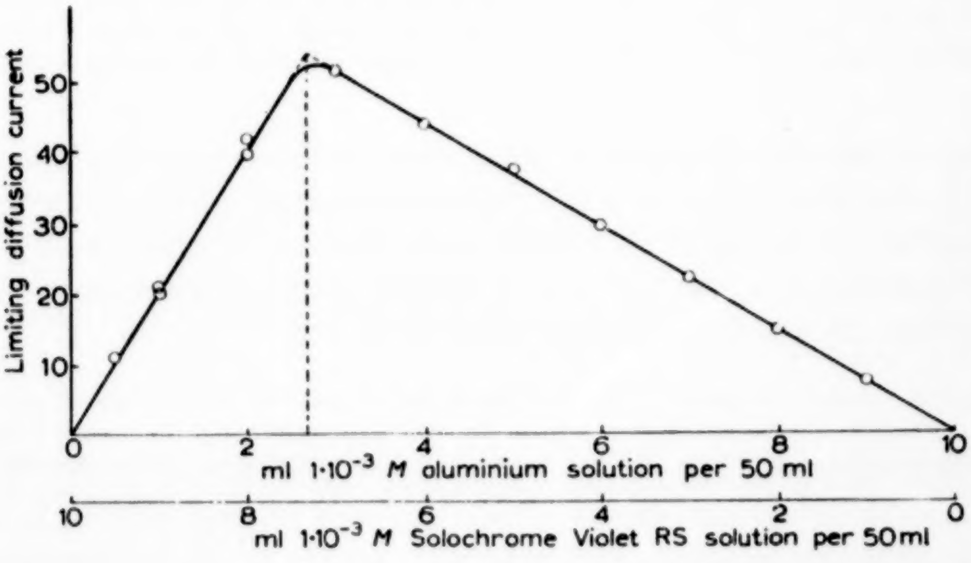

Fig. 6. Determination of the aluminium – solochrome violet R.S. ratio at pH 6.5. (JOB's method).

TABLE VII

Vol. $10^{-3}M$ dye solution added (ml)	*Vol. $10^{-3}M$ aluminium solution added (ml)*	*Peak height*[a] *(dye)*	*Peak height*[a] *(aluminium)*
9.5	0.5	43.5	11.0
9.5	0.5	43.5	8.5
9	1	26.5	21.0
9	1	23.5	20.0
8.5	1.5	6.5	30.0
8	2	6.0	42.0
8	2	4.5	40.0
7.5	2.5	—	41.0
7	3	—	51.0
6	4	—	44.0
5	5	—	37.0
4	6	—	29.5
3	7	—	22.0
2	8	—	14.5
1	9	—	7.0

[a] All peak heights for the free solochrome violet R.S. and for the aluminium solochrome violet R.S. species were recorded on the linear-sweep cathode ray polarograph using an impact load resistor (sensitivity control setting) of $1 \cdot 10^3$ ohms.

The intersection of the produced straight portions of the graph in Fig 6 occurred at a point equivalent to an aluminium: dye ratio of 2.675:7.325 (1:2.74). It was therefore concluded that the ratio of aluminium to dye in the species existing at pH 6.5 was 1:3.

Determination of half-wave potentials

For this determination, 50 ml of solution was prepared containing 4 μg/ml of aluminium, 0.01% solochrome violet R.S. and 0.2*N* with respect to ammonium acetate, was carefully adjusted to pH 4.60 in the usual manner. After heating for 10 min at 70°, the solution was cooled and an aliquot was deoxygenated and polarographed against a saturated calomel electrode. An external potentiometer and second calomel electrode were employed to measure the error due to the iR drop, which was, however, found to be negligible under the conditions adopted.
The following results were obtained:

$E_{1/2}$ (Solochrome violet R.S. at pH 4.60) = —0.269 V *versus* S.C.E.

$E_{1/2}$ (Aluminium – solochrome violet R.S. at pH 4.60) = —0.425 V *versus* S.C.E.

DISCUSSION

The experiments described above show that two distinct complex species are formed between aluminium and solochrome violet R.S. The first is stable in the pH range 4.2 to 5 and the second in the range 5.7 to 7. As stated earlier, the first of these species was reported by WILLARD AND DEAN[2] and was recommended by them for the determination of aluminium. It was employed by us for the determination of aluminium in beryllium[3]. No previous report of the second species is known.

The polarographic characteristics of a number of similar azo compounds is reported in the literature. Azobenzene is stated by TACHI[9] to reduce to hydrazobenzene by a process involving two electrons

$$\mathrm{ArN{=}NAr} + 2\mathrm{H}^+ + 2e \rightarrow \mathrm{ArNH{-}NHAr}.$$

It has been stated that this reaction is reversible at the platinized platinum microelectrode[10] and at the dropping mercury electrode[11]. WINKEL AND SIEBERT[12] have made extensive studies of the polarographic behaviour of azobenzene in relation to *cis-trans* isomerism. This work will be considered in greater detail in the next part in this series of papers.

The results obtained by us show that n, the number of electrons transferred per molecule reduced is 2 and 4 for the free dye and for the complex existing at pH 4.6, respectively. They also indicate that the reduction is similar to that of azobenzene. The shift of the half-wave potential with change of pH, obtained from the polarograms recorded in the preparation of Table I may be represented by the empirical equation

$$E_{1/2} = +0.66 - 0.07 \text{ pH}.$$

This is in good agreement with that obtained by WILLARD AND DEAN[2]. It is evident from this that, like azobenzene, hydrogen ion is involved in the reduction. The poor value of n, ($= 1.38$) however, obtained from the slope of a graph of applied voltage(E) *versus* $\log \frac{i}{id - i}$ indicates that the reaction is not, in this case, reversible. This conclusion is supported by the appearance of the small step, shown in Fig. 4, which appeared, as reported earlier, during the prolonged electrolysis of a small volume of a solution of the free dye. The half-wave potential of the step (-0.17 V) *versus* the mercury pool, was separated by about 0.3 V from the usual dye reduction step. It is suggested that it is due to the reduction of the azoxy derivative of the dye to the azo dye itself, the former being formed by anodic oxidation during the electrolysis. Anodic oxidation is possible in this case owing to the comparable area of the two electrodes used. The value for the diffusion coefficient of the free dye obtained ($0.48 \cdot 10^{-5}$ cm^2 sec^{-1}) is of the same order as that reported by CASTOR AND SAYLOR[11] for azobenzene, indicating that the value of 2 calculated for the electron transfer is correct. Values for the diffusion coefficient calculated assuming $n = 1$, 3 and 4 were $1.92 \cdot 10^{-5}$, $0.215 \cdot 10^{-5}$ and $0.12 \cdot 10^{-5}$ cm^2 sec^{-1} respectively. These are all widely different from those of similar compounds and the value of 2 is thus further supported.

The complex species formed in the presence of aluminium at pH 4.6 is shown to have a ratio of one aluminium to two dye molecules, which agrees with the findings of WILLARD AND DEAN[2]. The value of 4 electrons transferred in the reduction indicates that the two dye molecules are probably reducing by the mechanism already outlined, without modification by the complex formation. The value of $0.44 \cdot 10^{-5}$ cm^2 sec^{-1} obtained for the diffusion coefficient shows a small decrease compared with that of the dye, as would be expected in view of the larger size of the molecule. Calculations of diffusion coefficient assuming other values for n gave $7.05 \cdot 10^{-5}$, $1.76 \cdot 10^{-5}$, $0.78 \cdot 10^{-3}$ and $0.28 \cdot 10^{-5}$ cm^2 sec^{-1} for $n = 1$, 2, 3 and 5 respectively. It is obvious that none of these values is preferable to that assuming $n = 4$.

The shift of half-wave potential with pH, shown in Table I, may be represented by the empirical equation:

$$E_{1/2} = -0.24 - 0.06 \text{ pH}.$$

The agreement of this equation with that of WILLARD AND DEAN is also fairly good. Insufficient thermodynamic data are available for a reliable value of K, the stability of the complex to be calculated. It is hoped to deal with this problem more fully at a later stage in the work.

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The shift of half-wave potential with pH in heavily buffered media is predicted by:

$$E_{1/2} = E^{\circ} + \frac{RT}{nF} \cdot \ln \frac{K_R}{K_{RH}} + \frac{RT}{F} \cdot \ln \mathrm{H}^+$$

The expression $\frac{K_R}{K_{RH}}$ which is approximately equal to the ratio of the square roots of the diffusion currents is almost invariably so close to 1 that the term incorporating it is negligible[13]. A shift of 0.059 V per unit change of pH is therefore predicted. Agreement with this is close in the case of the complex and slightly less close of the free dye. Close agreement was not expected as the reactions are not likely to be reversible and the buffer capacity might not be sufficiently large.

The determination of the ratio of solochrome violet R.S. to aluminium at pH 6.5 gave a value of 3:1. In view of the rather unsatisfactory shape and separation of the two steps direct determination of electron transfer was not attempted. The ratio of the step height of the complex at this pH to that of the complex at pH 4.6 was approximately 3:2, indicating a value for *n* of 6. This assumed that the diffusion coefficient of this complex was not widely different from that of the free dye, or of the complex formed at pH 4.6. Assuming a value of 6 the diffusion coefficient was calculated to be $0.52 \cdot 10^{-5}$ cm^2 sec^{-1} which is of the expected order. A slightly smaller value would have been more likely in view of the size of this molecule, but this estimate is probably not an accurate figure, due to the difficulty encountered in precisely measuring the height of the rather poorly shaped step. Values assuming $n = 4, 5$ and 7 are $0.92 \cdot 10^{-5}$, $0.59 \cdot 10^{-5}$ and $0.3 \cdot 10^{-5}$ cm^2 sec^{-1} respectively, which are all much less likely to be correct. Complexing at pH 6.5 appears to offer a considerable increase in sensitivity for the determination of aluminium, but the steps obtained are more difficult to measure than those obtained at pH 4.6. Measurement is much easier when the cathode ray polarograph is employed, but in view of the already great sensitivity obtained it does not appear likely that determination at pH 6.5 would really offer marked advantage.

Although the work described in this paper has provided data concerning the combining ratios of the complexes and the probable reduction mechanism, no attempt has been made to elucidate the structure, or the type and position of substituent groups essential for complexing. Studies of metal-azo dye complexes have, however, been reported in the literature and, in particular, the copper complexes have been investigated by PFITZNER[14], JONASSEN AND WILSON[15] and BAILER, CALLIS *et al.*[16,17]. Complexes with magnesium[18] and vanadium[19] have also received some attention.

In order to make a comparative study of the aluminium complexes it was considered necessary to examine the polarographic characteristics of dyes other than solochrome violet R.S. and the effect of the presence of aluminium upon them. Preliminary studies of this nature will be presented and discussed in the next part of this series of papers.

SUMMARY

A study of the behaviour of the aluminium–solochrome violet R.S. complex is made over the range pH 1.95 to 10.08 and it is shown that two distinct complexes are formed. Determinations of the number of electrons per molecule transferred in the reduction of these complexes are made and values for the ratios of dye to aluminium are also obtained. The results are discussed and compared with those of other workers. Some conclusions are presented.

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Received September 27th, 1957

THE CONDUCTOMETRIC TITRATION OF CARBOXYLIC AND PHENOLIC ACIDS IN NON-AQUEOUS SOLUTIONS

I. PRELIMINARY EXPERIMENTS

by

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INTRODUCTION

The titration of acids and bases in non-aqueous media has so far been carried out chiefly with the aid of the potentiometric and high-frequency techniques[1–5]. Notwithstanding the successful results that are frequently obtained with these methods, they cannot in all cases be regarded as ideal.

In the *potentiometric technique* trouble is frequently caused by the fact that the electrodes are in contact with the solution. The glass electrode generally used as indicator electrode is liable to attack by common reagents, notably by potassium and sodium ions. Furthermore, the formation of precipitates often hampers the execution of the titration.

In the *high-frequency technique* these difficulties are eliminated by using external electrodes. This can be done because the method is essentially based on the determination of dielectric losses, for which purpose a direct contact between electrodes and solution is not essential. A disadvantage of this procedure is, however, that it requires relatively complicated apparatus.

This is not the case with direct *conductometric titration*, which is based on a largely analogous principle, *viz.*, the measurement of the electrical resistance of the solution during titration. In this method the electrodes are immersed in the solution, but here (as opposed to the potentiometric procedure) this practice generally does not affect the accuracy.

One motive for the present study of conductometric titrations in non-aqueous solutions was therefore a practical one: the possible substitution of this simple technique (instead of the more complicated high-frequency procedure) in cases where the potentiometric method gives rise to difficulties.

Another reason for carrying out the investigation was the hope that it would afford some insight into the ionization equilibria occurring in non-aqueous media during the course of titration. Such an insight would be of value not only in applying the conductometric method itself, but would also give a better understanding of the fundamentals underlying potentiometric titrations. On this account, the solvents and titrant solutions chosen in the present investigation have been mainly the same as those used in a previously reported study on potentiometric titration[2,3].

The present paper is chiefly a preliminary account of the experience gained in practice with conductometric titrations in non-aqueous media. It is the authors' intention to deal with the more fundamental insight gained during this investigation in a second publication, whilst the more general analytical application of the conductometric method will be discussed in a third paper.

EXPERIMENTAL

Titrant solutions and solvents

Two bases were used in the experiments, *viz.*, a solution of potassium methoxide in pyridine–benzene, as described by LIPPMAA[6] and tetramethylammonium hydroxide in methanol–benzene. The strength of both titrants was *ca.* 0.3*N*.

The first base was prepared by carefully dissolving 6.5 g of metallic potassium in a mixture of 70 ml methanol and 30 ml benzene and making up the solution to 400 ml with pyridine.

The second base was prepared by the conversion of tetramethylammonium iodide into the hydroxide by reaction with freshly prepared (carbonate-free) silver oxide in methanol. The solids were filtered off and the solution was made up to the required strength with the same volume of benzene.

All operations were carried out with careful exclusion of atmospheric carbon dioxide by means of nitrogen. As solvents, methanol, pyridine and dimethylformamide (DMF) were generally used. They were of reagent grade and contained less than 0.5% water.

Electrical equipment

The resistance measurements were carried out with a Philips conductivity bridge, GM 4249/01, used in conjunction with an external decade-type resistance box, ranging from 10 × 1 to 10 × 100,000 ohms.

The bridge was operated at either 50 or 1000 c/sec, the lower frequency being used for resistances of the order of $10^5 \Omega$ and higher, the latter for lower resistances.

The resistance range was in general from 1000 Ω to 100 kΩ, except in the case of solutions of acids in pyridine or DMF. For these solutions, the initial resistance was of the order of 1 megohm.

Corrections for capacitance effects were made on the instrument.

For the electrode system we used the dip-type measuring assembly GM 4221, consisting of platinized platinum electrodes. The cell constant was about 1.

No particular difficulties were encountered in the use of ordinary platinum electrodes. Indeed, in none of the titrations were we confronted with problems due to the electrode material used.

The relative accuracy obtained in the measurements was *ca.* 0.1% and was equal to the absolute accuracy of the resistance box.

Titration procedure

The acids were weighed accurately in a 50-ml beaker (tall form) in such amounts that 1 to 2 ml of 0.3*N* base was required per acid group of compound to be determined. 25 ml of solvent was then added, the electrode assembly inserted and the magnetic stirrer started.

After dissolving the acid, the base was added by means of a semi-micro burette (10 ml) in 1/10 ml portions and the equilibrium reading of the bridge was taken after each addition.

In most titrations, equilibrium was reached within half a minute. When a precipitate was formed, however, equilibrium was sometimes reached very slowly. Under these circumstances, readings were taken at two- or three-minute intervals.

No special thermostatic control was applied, but it proved advisable to work in a room of approximately constant temperature.

RESULTS FOR VARIOUS ACIDS

Members of the following five groups of organic acids were studied:

A. Aliphatic monocarboxylic acids.
B. Aromatic monocarboxylic acids.
C. Aliphatic dicarboxylic acids.
D. Aromatic dicarboxylic acids.
E. Alkylphenols and derived phenols.

The results of the titrations are summarized in Table I.

A. Aliphatic monocarboxylic acids

The acids investigated could be titrated in pyridine and DMF both with potassium methoxide and with tetramethylammonium hydroxide. Methanol was not suitable for these acids, as no breaks in the titration curves could be obtained. Pyridine gave slow precipitate formation with the methoxide base, but good results were found with the other base.

In general dimethylformamide as a solvent gave better results; only caproic acid could not be titrated in this solvent with tetramethylammonium hydroxide. Figs. 1 and 2 give examples of the titration curves for these acids. As in the other figures, the units of the ordinate are conductance units.

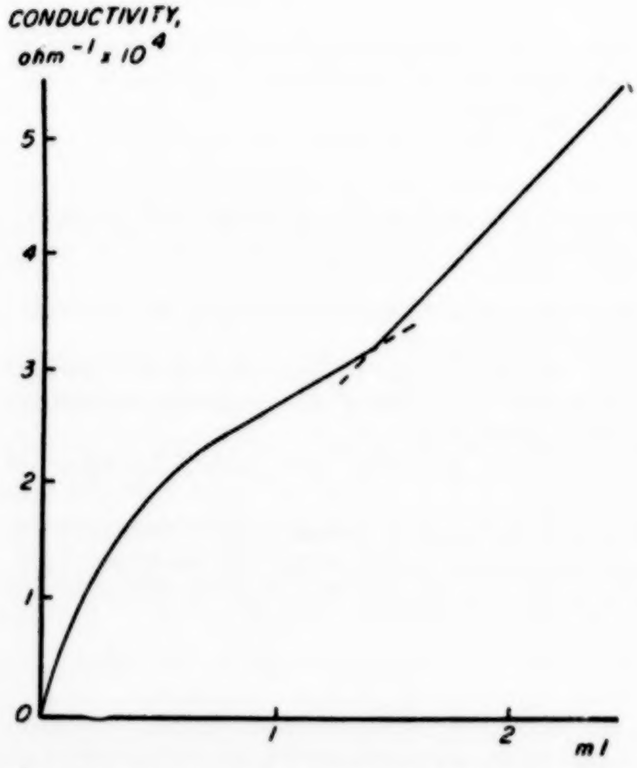

Fig. 1. Titration of formic acid in pyridine with tetramethylammonium hydroxide.

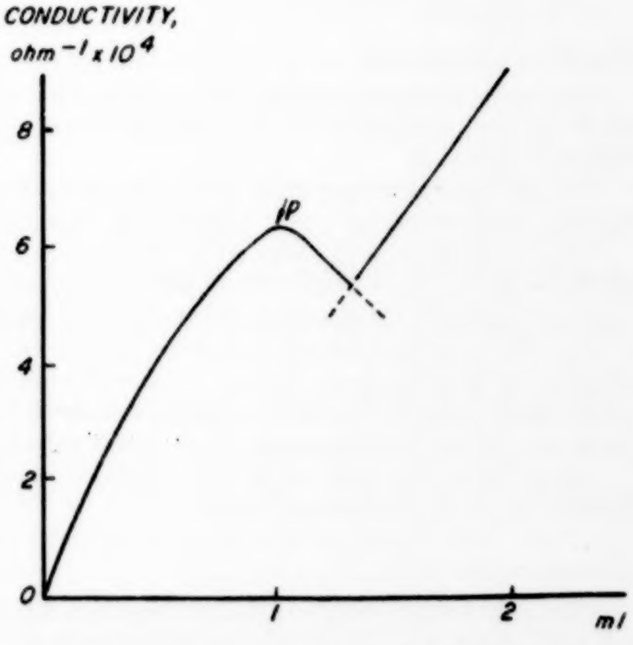

Fig. 2. Titration of acetic acid in dimethylformamide with potassium methoxide (p=precipitate formation).

TABLE I

Acids		*Titrant: Potassium methoxide*			*Titrant: Tetramethylammonium hydroxide*			
		Solvents			*Solvents*			
Groups	*Compounds*	*Methanol*	*Pyridine*	*Dimethylformamide*	*Methanol*	*Pyridine*	*Dimethylformamide*	*Binary mixtures*
Aliphatic monocarboxylic acids	formic acid	—	—	+ p	—	+	+	
	acetic acid	—	+ p	+ p	—	+	+	
	caproic acid	—	+ p	+ p	—	+	—	
Aromatic monocarboxylic acids	benzoic acid	—	—	+ p	—	—	—	
	salicylic acid	+	+ p	+ p	—	—	—	
	p-hydroxybenzoic acid	—	—	+ p	—	—	—	
Aliphatic dicarboxylic acids	oxalic acid	+ p	—	—	+	—	+ p	MeOH–DMF; MeOH–pyr.
	malonic acid	+	—	+ p	+	+ p	+ p	MeOH–DMF
	succinic acid	+	—	+ p	+	+ p	+	
	adipic acid	+	+ p	+ p	+	+ p	+	
	fumaric acid	+ p	—	+ p	+	+ p	+	
	maleic acid	+	+ p	+ p	+	+ p	+	
	tartaric acid	+ p	—	—	+	—	+	
Aromatic dicarboxylic acids	phthalic acid	+	—	+ p	+	+ p	+	
	isophthalic acid	+	—	—	+	+ p	+	Benz.–pyr.; MeOH–DMF; pyr.–DMF
	terephthalic acid	—	—	—	+	+ p	+ p	(Benz.–pyr.)$_p$
Alkylphenols and derived phenols	phenol	—	+	—	—	—	—	
	cresols	—	+	—	—	—	—	
	xylenols	—	+	—	—	—	—	
	o-nitrophenol	—	+	—	—	—	—	
	p-nitrophenol	—	+ p	+	—	+	+	

+ = determination of the equivalence point(s) by conductometric titration is possible (— = not possible).
p = precipitate formation.

B. Aromatic monocarboxylic acids

These acids could only be titrated with potassium methoxide. DMF was the solvent in which the best results were obtained, notwithstanding the occurrence of a precipitate. As this precipitate was formed fairly quickly, this solvent did not give rise to serious difficulties. The determination of salicylic acid in pyridine, which is also accompanied by precipitate formation, caused more trouble after the second equivalence point, somewhat long interval readings being necessary in this part of the titration. However, both equivalence points could be determined accurately. In methanol, the titration curve showed only an indistinct break and the determination of the equivalence point was fairly poor.

Unlike salicylic acid, *p*-hydroxybenzoic acid showed only one clear equivalence point in dimethylformamide. The second one could not be used analytically, because of its obscurity.

The occurrence of two equivalence points for both hydroxybenzoic acids is caused by the insolubility of the bipotassium salts of these compounds, the monopotassium salts being soluble. Fig. 3 shows the titration curve of salicylic acid in dimethylformamide.

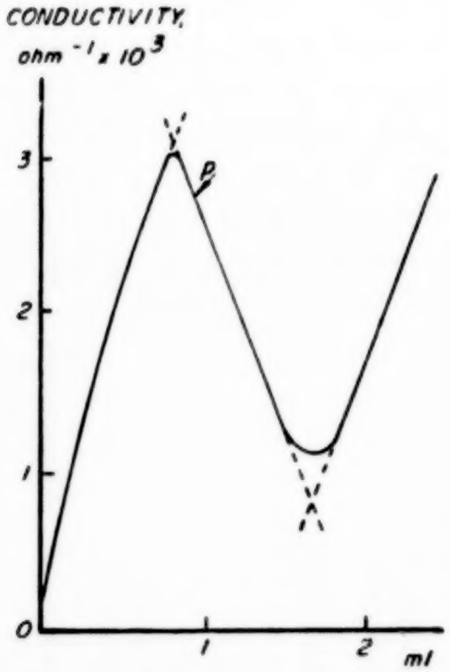

Fig. 3. Titration of salicylic acid in dimethylformamide with potassium methoxide (p = precipitate formation).

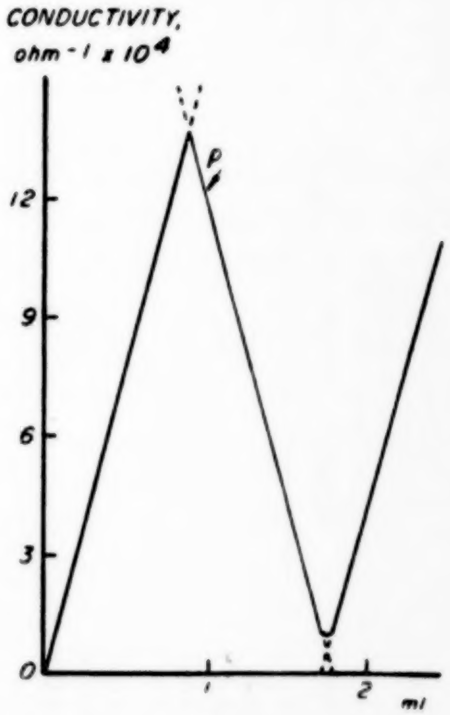

Fig. 4. Titration of oxalic acid in dimethylformamide with tetramethylammonium hydroxide (p = precipitate formation).

C. Aliphatic dicarboxylic acids

All these acids could be successfully titrated, both with potassium methoxide in methanol and with tetramethylammonium hydroxide in methanol or dimethylformamide. Moreover, most of them could be determined with potassium methoxide in dimethylformamide, and, with the other base, also in pyridine.

Figs. 4 and 5 show the titration curves for oxalic acid with tetramethylammonium hydroxide and for maleic acid with potassium methoxide respectively, both titrations being carried out in dimethylformamide. In these titrations the N-shaped curves, like the one for salicylic acid, are caused by precipitate formation immediately after the first equivalence point. When no precipitate was formed, however, curves like the one in Fig. 6 were obtained. In this figure, the result is given of the titration of succinic acid with potassium methoxide in methanol.

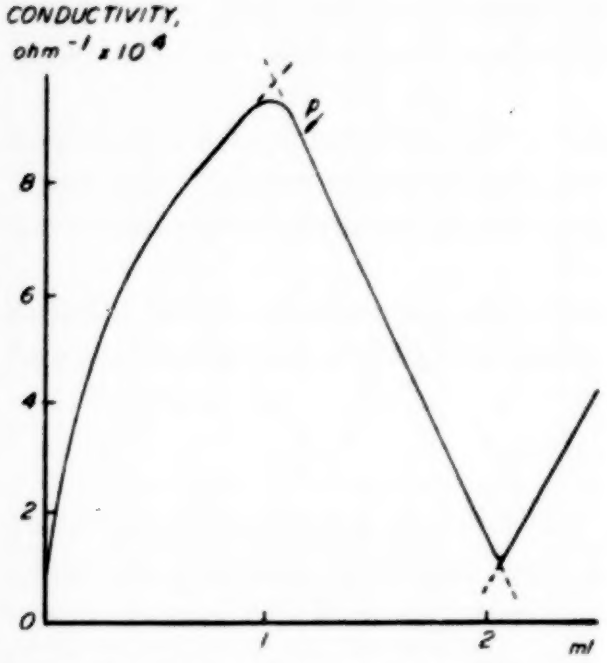

Fig. 5. Titration of maleic acid in dimethylformamide with potassium methoxide (p = precipitate formation).

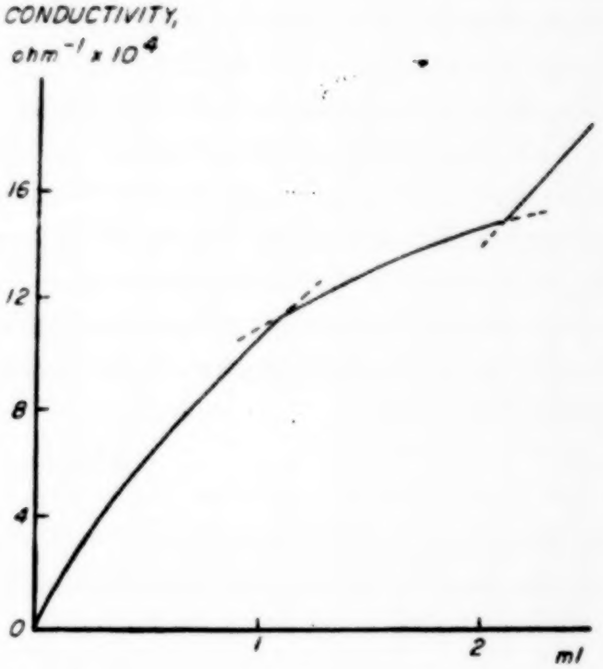

Fig. 6. Titration of succinic acid in methanol with potassium methoxide.

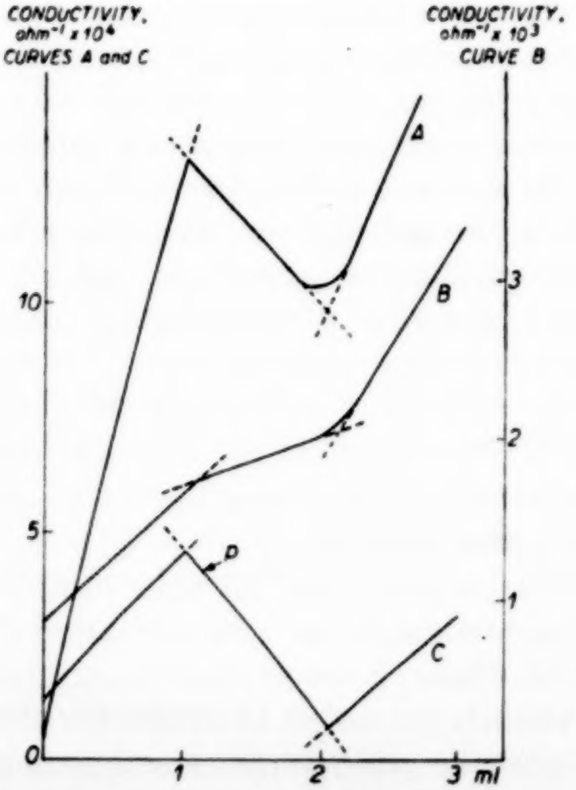

Fig. 7. Titration of maleic acid in different solvents with tetramethylammonium hydroxide. A in DMF, B in methanol, C in pyridine (p = precipitate formation).

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In Fig. 7 the influence of the solvent on the titration curve is demonstrated for maleic acid, titrated with tetramethylammonium hydroxide. The same behaviour was found for malonic acid. From the curves obtained it is seen that their shape is highly dependent on the properties of the solvent. In pyridine, the titration curve shows the sharpest breaks and thus the equivalence points can be determined very accurately in spite of the precipitate formation. In methanol the breaks are less pronounced. In dimethylformamide the determination of the first equivalence point does not present difficulties, but the second is less easy to find, the curve being considerably rounded off at this point.

The most noteworthy feature of these results is the occurrence of an N-shaped titration curve in dimethylformamide without precipitate formation. The same phenomenon was observed by HIGUCHI AND REHM[7] in the titration of sulphuric acid in acetic acid with alkali acetates.

According to these authors the initial increase in the conductance of the solution is due to the higher degree of ionization of the alkali bisulphates into alkali ions and bisulphate ions:

$$MHSO_4 \rightleftarrows M^+ + HSO_4^-$$

as compared with the sulphuric acid molecules. The decrease following neutralization of the first hydrogen ion can be ascribed to the lower degree of ionization of the alkali sulphate, according to

$$M_2SO_4 \rightleftarrows 2\ M^+ + SO_4^{-2}$$

as compared with the ionization of the alkalibisulphate.

Similar curves were obtained by MASUI[8] in the high-frequency titration of organic dicarboxylic acids in non-aqueous media with sodium methoxide.

The explanation for the shape of the titration curve in both the conductometric titration of maleic acid in dimethylformamide and the high-frequency titrations by MASUI is probably the same as that given by HIGUCHI AND REHM.

In the titrations of dicarboxylic acids in pyridine with tetramethylammonium hydroxide, a precipitate was formed after the first equivalence point, causing a decrease in conductance. As a matter of fact, the explanation given by HIGUCHI AND REHM is only valid for titrations in which no precipitate is formed.

In general, we can say that unless a precipitate is slowly formed, titration of the aliphatic dicarboxylic acids can best be performed in pyridine or dimethylformamide.

D. Aromatic dicarboxylic acids

From this group we studied the three isomeric *o*-, *m*- and *p*-phthalic acids, *viz.* phthalic, isophthalic and terephthalic acid.

In general, the phthalic acids could only be titrated with tetramethylammonium hydroxide; with potassium methoxide the slow formation of a precipitate too often took place. Using the former base, however, satisfactory results were obtained, not only with phthalic acid, which is the easiest to titrate, but also with the other isomers.

The titration curve of phthalic acid with tetramethylammonium hydroxide shows two breaks in all solvents used. The influence of the medium is the same as for maleic and malonic acid (Fig. 8).

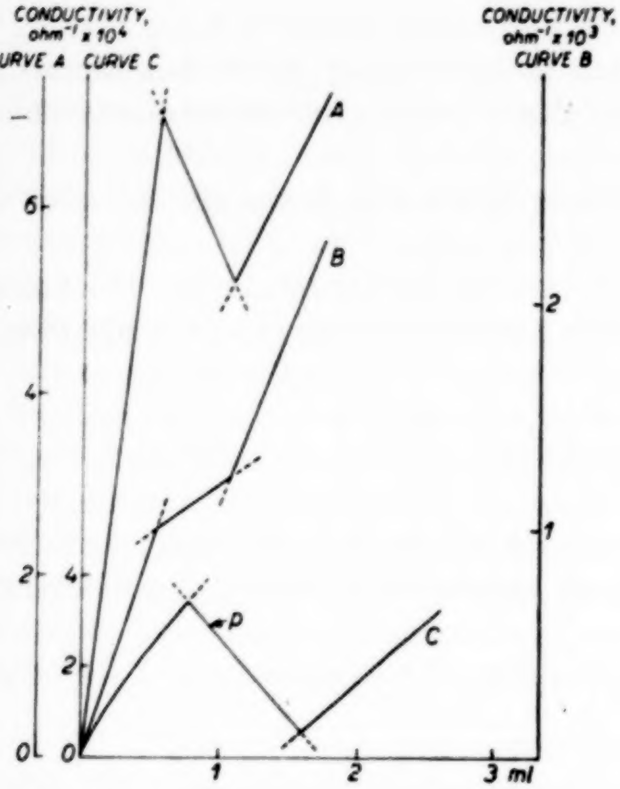


Fig. 8. Titration of phthalic acid in different solvents with tetramethylammonium hydroxide. A in DMF, B in methanol, C in pyridine (p = precipitate formation).

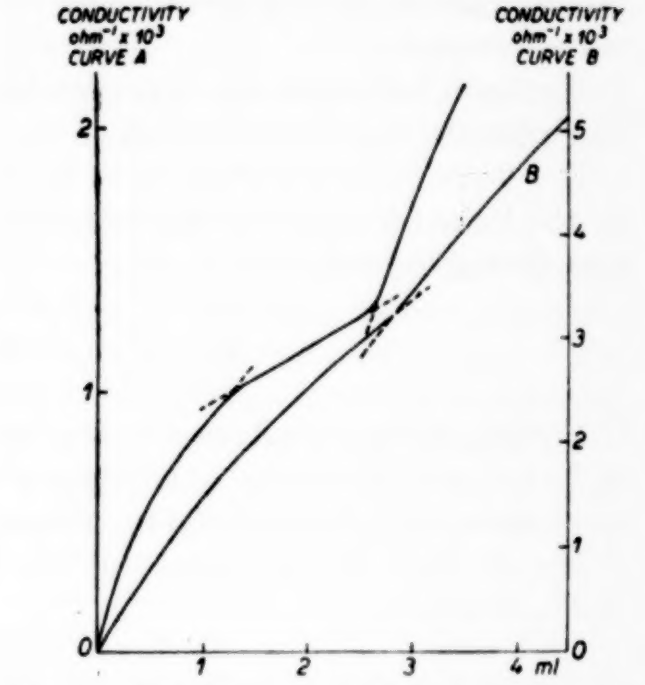


Fig. 9. Titration of isophthalic acid in different solvents with tetramethylammonium hydroxide. A in pyridine–DMF, 16:4 (v/v), B in DMF.

The titration curve of isophthalic acid often shows only one break, but in a suitable solvent mixture, two equivalence points may be obtained. For example, in the pure solvents methanol, dimethylformamide and pyridine, only one clear break is found, though in dimethylformamide there are indications that a second may be present. If, however, a mixture of pyridine and dimethylformamide (volume ratio 16:4) is used, both breaks are sharper and the first equivalence point can also be determined with fair accuracy (Fig. 9).

Terephthalic acid could only be titrated with tetramethylammonium hydroxide, but nevertheless a precipitate is immediately formed in all solvents used. Generally, precipitation occurs slowly, necessitating the taking of readings at timed intervals.

In the pure solvents, the end-points were not sharply defined. Solvent mixtures of dimethylformamide and pyridine were then used and it was observed that the sharpness of both equivalence points increased with the pyridine concentration. The best results, however, were obtained with pyridine–benzene mixtures (Fig. 10). During the initial slow formation of the precipitate, readings were taken every two minutes. In this titration an inflection was observed between the first and the second equivalence point, but this has no analytical significance. The accuracy of this determination under optimum conditions (volume ratio pyridine: benzene = 2:1) is of the order of 1%.

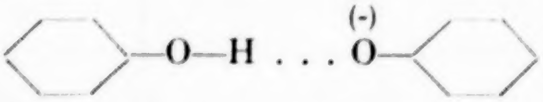
E. Alkylphenols and derived phenols

The alkylphenols could only be titrated with potassium methoxide, using pyridine as a solvent. The use of mixtures of pyridine, DMF and diethylamine, as reported by LIPPMAA[6], did not improve the titration.

All members of the alkylphenol group showed the same titration curve (Fig. 11). From this it is seen that a maximum in the conductance occurs before half-neutralization, followed by a decrease up to the equivalence point, after which the conductance rises again.

The same behaviour was observed by Lippmaa in the high-frequency titration of alkylphenols under these conditions.

The shape of the titration curve has not yet been accounted for. It may be caused by the formation of complexes between the free phenol molecules and the phenolate ions during the titration[3,9].



If alcohol-containing solvents and/or bases are used (*cf.* the high-frequency titration of Lane[5] and Karrman and Johansson[10]) no maximum is observed, which is in accordance with the explanation offered.

The accuracy in the conductometric determination of alkylphenols is of the order of 2% (relative).

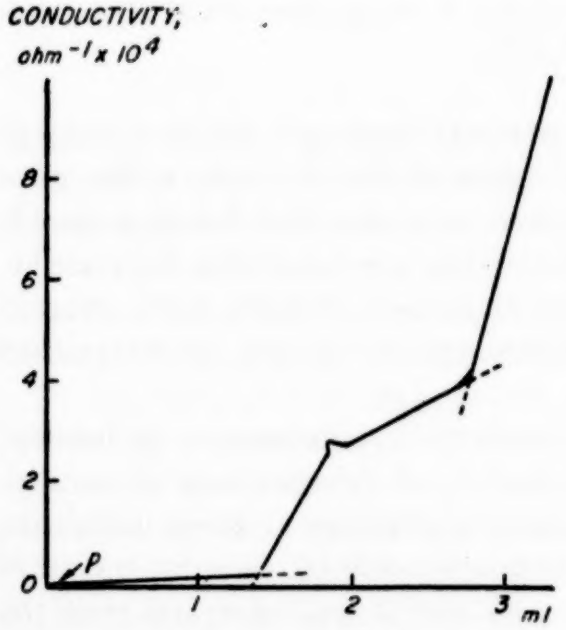


Fig. 10. Titration of terephthalic acid in pyridine–benzene, 14:6 (v/v) with tetramethylammonium hydroxide (p = precipitate formation).

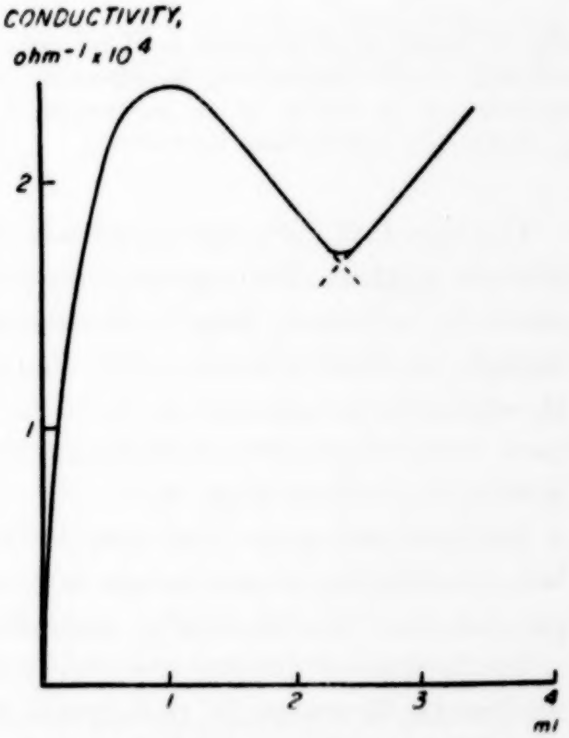


Fig. 11. Titration of 3.5-xylenol in pyridine with potassium methoxide.

Of the nitrophenols, the *ortho*-isomer could only be titrated in pyridine, using potassium methoxide. For the determination of the *para*-isomer, tetramethylammonium hydroxide could also be used.

The shape of the curves is the same as that obtained with the monocarboxylic acids (Fig. 1). This was to be expected, because the acid strengths of nitrophenols and monocarboxylic acids are of the same order.

Consequently, the determination of the equivalence points in these titrations is not as accurate as, for instance, that of dicarboxylic acids.

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CONCLUSIONS

In addition to the potentiometric and high-frequency titration methods, another electrochemical technique, the conductometric end-point determination, has proved to be applicable in many cases for acid-base titrations.

The apparatus used was simple, consisting of a commercial conductivity bridge in conjunction with an external decade-type resistance box. In this way a sufficient degree of accuracy was obtained.

From the results it is concluded that conductometric titrations in non-aqueous solutions are most successful in the case of dicarboxylic acids and may offer special advantages over the potentiometric determination. Under favourable conditions, monocarboxylic acids and phenols can also be titrated conductometrically. Of the two bases employed, tetramethylammonium hydroxide in general gave the best results. This base gave less precipitate formation and, if any precipitate was formed, satisfactory titrations were still possible, Potassium methoxide gave precipitates in most titrations but could be used with success, especially in the determination of phenols.

ACKNOWLEDGEMENT

The authors are much indebted to Miss A. SNIP who skilfully carried out many of the experiments. They wish to express their gratitude to DR. IR. P. N. DEGENS Jr. for his stimulating interest in this investigation.

SUMMARY

The present study deals with the conductometric titration of weak organic acids and alkylphenols in non-aqueous solution.

It is shown that the results are highly dependent on the bases and solvents used. A detailed account is given of experience gained with this method.

A series of successful titrations of some types of acids is described in order to illustrate the versatility of conductometric titration.

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Received October 22nd, 1957

INFLUENCE DE LA CINÉTIQUE DES RÉACTIONS CHIMIQUES SUR LES COURBES DE POLARISATION*

APPLICATION À L'ÉTUDE DES COMPLEXES THIOCYANÉS DU TITANE(IV) ET DU TITANE(III)

par

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INTRODUCTION

Soit le couple oxydo-réducteur des 2 ions A et A'

$$A + ne \rightleftarrows A'$$

auquel on ajoute un excès d'ions B non électroactifs susceptibles de former les complexes AB^b et $A'B^{b'}$. Ces complexes constituent un deuxième couple oxydo-réducteur:

$$AB^b + (b'-b)B + ne \rightleftarrows A'B^{b'}$$

Les vitesses d'oxydation et de réduction à l'électrode sont généralement différentes pour les deux couples. Nous considérerons les deux cas extrêmes:
(1) les ions simples sont beaucoup plus actifs que les complexes;
(2) les ions complexes sont beaucoup plus actifs que les ions simples;
et nous supposerons l'électrolyse rapide devant les autres phénomènes.

Dans les deux cas, en présence d'un excès d'électrolyte indifférent, l'espèce active qui disparait électrochimiquement est remplacée, à l'électrode, par les deux phénomènes suivants: la diffusion de cette espèce active depuis le sein de la solution, (qui dépend de son degré de formation) et sa reformation chimique (qui dépend des constantes cinétiques). La concentration de l'ion complexant agit en général sur ces phénomènes. De plus, dans le deuxième cas, elle influence directement la réaction d'électrolyse.

Lorsque les réactions chimiques à l'électrode sont très rapides devant la diffusion des espèces présentes, une seule vague est observable; elle est due à l'oxydo-réduction du système le plus électroactif. La vitesse de diffusion limite seule le courant et si cette vitesse est la même pour le complexe et l'ion simple, le courant limite est constant quel que soit le degré de formation du corps actif; tout se passe comme si la totalité de A ou de A' était sous la forme électrolysée. La plupart des études de complexes par voie polarographique concernent des réactions chimiques rapides — supposées de plus quantitatives dans le sens de la formation des complexes; ces derniers sont donc assez stables.

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* Un résumé de ce travail a éte présenté en communication au XVème Congrès International de Chimie Pure et Appliquée, Lisbonne, 1956.

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L'autre cas extrême est celui où les réactions chimiques sont tellement lentes qu'elles n'interviennent plus. Les espèces A et AB^b se comportent alors comme deux oxydants indépendants — 2 vagues peuvent être observées si les potentiels normaux des deux couples sont assez différents. Le courant est toujours limité par la diffusion, mais cette fois, seule, celle de l'espèce active intervient; la vague correspondante disparaît donc quand la formation chimique de l'espèce active est nulle.

Entre ces domaines extrêmes, des termes de cinétique chimique peuvent apparaître dans l'expression du courant limite et du potentiel de demi-vague.

Nous allons examiner comment se composent les différents phénomènes et voir quelle contribution peut apporter à la connaissance des complexes, l'étude des deux variables intensité limite et potentiel de demi-vague, en fonction de la concentration de l'ion complexant.

Nous commencerons par l'étude du courant limite dans certains cas particuliers simples, étude qui permet d'analyser les phénomènes à l'électrode, nous donnerons ensuite l'expression générale de ce courant, puis celle du potentiel de demi-vague.

Les travaux antérieurs concernant la cinétique seront signalés dans les paragraphes correspondants.

Enfin, nous présenterons les résultats obtenus au cours de l'étude expérimentale des complexes thiocyanés du titane(IV) et du titane(III) — résultats qui illustrent le premier cas considéré théoriquement ci-dessous.

Nous nous limiterons à l'étude de la vague du corps le plus actif à l'électrode.

I. LES COMPLEXES SONT PLUS ÉLECTROACTIFS QUE LES IONS SIMPLES

Une seule oxydo-réduction à l'électrode dans le domaine de potentiel considéré:

$$AB^b + (b'-b)B + ne \rightleftarrows A'B^{b'}$$

A. Étude simplifiée des courants limites

Prenons l'exemple du courant cathodique, négatif par convention. La vitesse d'électrolyse est égale à la vitesse de diffusion du complexe augmentée de la vitesse de formation chimique de ce même complexe.

$$-i_c = k_d\mathrm{Ox} + k_{\mathrm{ox}}B^bA_{\mathrm{el}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Ox: concentration du complexe oxydant dans la solution;
A_{el}: concentration de l'ion simple à l'électrode;
k_d et k_{ox} sont respectivement la constante de diffusion de la relation d'Ilkovic et la constante apparente de vitesse de formation du complexe. Ces deux constantes dépendent du dispositif expérimental (p. 78).

Comparons les vitesses maxima que peuvent prendre les deux phénomènes, indépendamment l'un de l'autre, c'est-à-dire les expressions:

$$k_d\mathrm{Ox} \text{ et } k_{\mathrm{ox}}B^bA = k_A\mathrm{Ox}$$

(k_A: constante apparente de vitesse de dissociation). Le rapport de ces vitesses $\dfrac{k_d}{k_A}$ est indépendant de la concentration de l'ion complexant. Il est constant pour un système et un dispositif expérimental donné.

Considérons les deux cas extrêmes:

1. *La mise en équilibre chimique du complexe est lente devant sa propre diffusion*:

$$k_A \ll k_d \text{ ou } k_{ox}B^bA \ll k_d\text{Ox}$$

Dans ce cas, étant donné que A_{el} ne peut être qu'inférieur ou égal à A, le courant limite se réduit à:

$$-\,i_c = k_d\text{Ox} = k_d \frac{c}{1 + \dfrac{K_1}{B^b}}$$

On peut considérer qu'il n'y a pas équilibre entre le complexe et l'ion simple. La vague du complexe n'est observable que s'il existe suffisamment dans la solution.

L'intensité limite permet de déterminer la constante de diffusion k_d lorsque la réaction est quantitative et la constante de dissociation $K_1 = \dfrac{A.B^b,}{Ox}$ lorsque la réaction n'est pas quantitative.

2. *La mise en équilibre chimique du complexe est rapide devant sa propre diffusion*:

$$k_A \gg kd \text{ (Fig. 1)}$$

Le terme cinétique de l'intensité n'est plus négligeable. Il faut tenir compte d'un troisième phénomène: le mouvement des ions simples vers l'électrode. Ceux-ci dis-

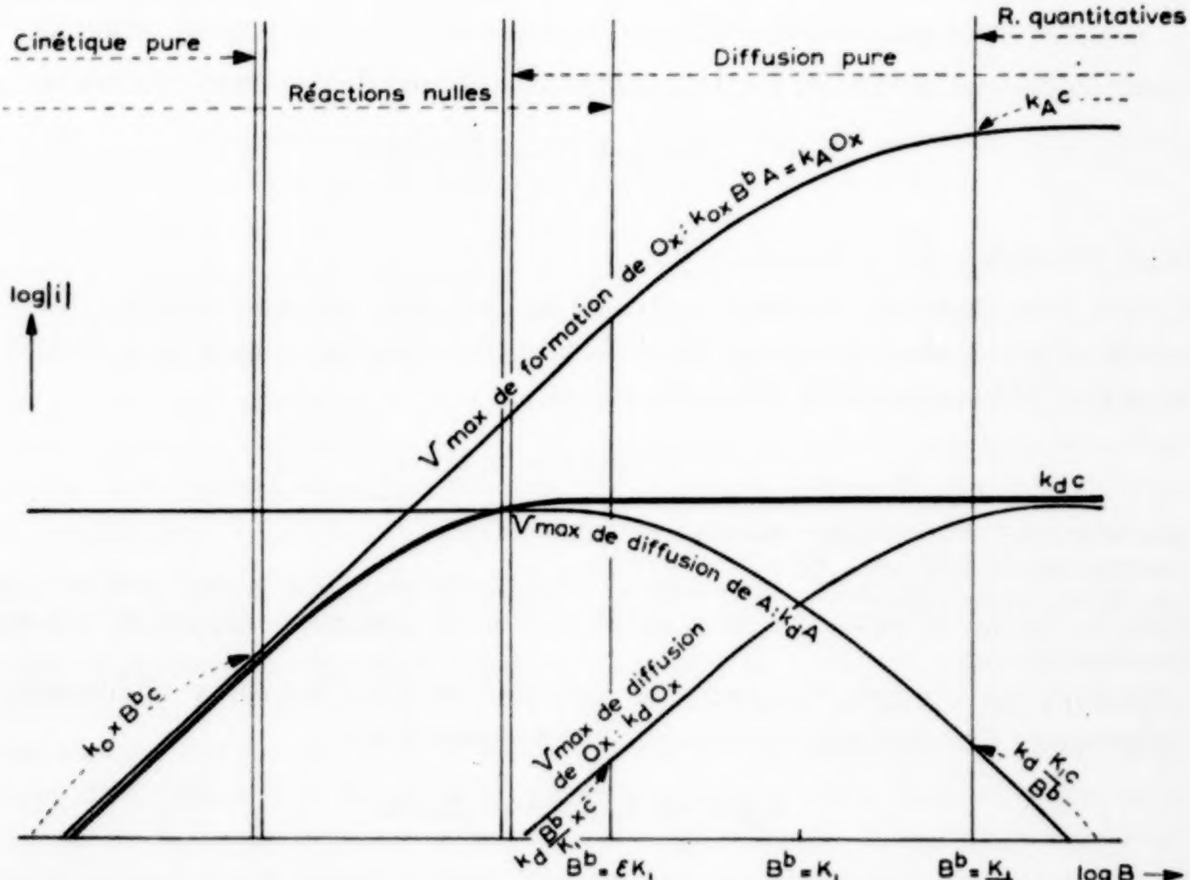

Fig. 1. Complexes électroactifs. ——— = variation de l'intensité limite cathodique en fonction de la concentration de l'ion complexant lorsque les réactions chimiques sont rapides devant la diffusion du complexe. ($k_A \gg k_d$). On suppose $k_d = k_{d_{(A)}}$.
Ox = complexe actif; A = ion simple inactif; k_{ox} = constante apparente de formation du complexe actif; k_A = constante apparente de formation de l'ion simple inactif.

paraissent par réaction chimique et sont remplacés par diffusion; on a donc, en désignant par $k_{d(A)}$ la constante de diffusion des ions A:

$$k_{ox}B^b A_{el} = k_{d(A)}(A - A_{el}) \quad \ldots \ldots \quad (2)$$

le plus lent des deux phénomènes limite le déplacement des ions simples; les vitesses maxima sont $k_{ox}B^bA$ et $k_{d(A)}A$ et, cette fois, le rapport des vitesses dépend de la concentration de l'ion complexant.

(a) Lorsque cette concentration est assez élevée pour que la réaction chimique soit rapide vis-à-vis de la diffusion des ions simples, la diffusion seule limite le courant ($k_{ox}B^b \gg k_{d(A)}$)

$A_{el} = 0$ comme Ox_{el} et
$-i_c = k_dOx + k_{d(A)}A$
$i_c = i_{max(ox)}$, si la réaction chimique est quantitative
$i_c = i_{max(A)}$, si la réaction chimique est nulle,

mais, si les deux constantes de diffusion sont égales, les deux valeurs précédentes sont confondues et:

$$-i_c = k_dc = -i_{max}$$

On observe alors la même intensité limite, que le complexe soit formé ou non, ceci parce que les ions libres diffusent comme ce dernier, à la suite du déplacement rapide de l'équilibre chimique. La vitesse de formation du complexe actif à l'électrode atteint alors la valeur maximum autorisée par la diffusion.

(b) Si l'on fait diminuer suffisamment la concentration de l'ion complexant, la vitesse maximum de formation du complexe devient très inférieure à la vitesse maximum de diffusion des ions libres ($k_{ox}B^bA \ll k_{d(A)}A$). Elle limite alors seule le courant qui est faible par rapport au courant maximum, mais supérieur à ce qu'il serait en l'absence de génération chimique de l'oxydant. La concentration de l'ion simple à l'électrode est confondue avec la concentration en solution et cette dernière, avec la concentration totale c:

$$-i_c = k_{ox}B^bA = k_{ox}B^bc$$

car la réaction chimique est obligatoirement nulle lorsqu'on se trouve en présence d'une vague cinétique. En effet, on a les deux conditions:

$$k_A \gg k_d$$

$$\text{et } k_{ox}B^bA \ll k_{d(A)}A \text{ ou } \frac{B^b}{K_1} \ll \frac{k_{d(A)}}{k_A} \text{ (en remplaçant } k_{ox} \text{ par } \frac{k_A}{K_1}\text{)}$$

$\frac{B^b}{K_1}$, c'est à dire $\frac{Ox}{A}$, rapport des concentrations du complexe et de l'ion simple est donc inférieur à une constante beaucoup plus petite que 1.

(c) Dans le domaine intermédiaire, où la diffusion des ions simples et la cinétique interviennent à la fois, la réaction chimique est déjà nulle, mais il est nécessaire d'évaluer A_{el} d'après la relation (2). En portant la valeur trouvée dans l'expression du courant (1), on obtient:

$$-i_c = k_{d(A)}\,c\,\frac{B^b}{B^b + \frac{k_{d(A)}}{k_{ox}}} = i_{max_A}\frac{B^b}{B^b + \frac{k_{d(A)}}{k_{ox}}}$$

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expression générale de l'intensité limite dans le cas (2) tant que la réaction chimique reste nulle.

La variation de l'intensité limite en fonction de la concentration de l'ion complexant est représentée sur la Fig. 1. Sur cette figure, sont portées aussi les vitesses maxima des phénomènes qui participent à l'ensemble du mécanisme:
diffusion du complexe oxydant, diffusion des ions libres et réaction chimique. Les deux constantes de diffusion sont supposées égales.

La courbe $\log |i_c| = f(\log \mathrm{B})$ traduit le passage du domaine de diffusion pure à celui de cinétique pure. La position des domaines de réaction quantitative et de réaction nulle est qualitativement celle que nous avons rencontrée au cours de l'étude expérimentale (p. 86).

De l'ensemble de la courbe de la Fig. 1 on déduit les valeurs de la constante de diffusion dans le domaine de diffusion pure — de la constante de formation et surtout du nombre *b* d'ions complexants figurant dans le complexe, dans le domaine où intervient la cinétique.

Remarque

Lorsque la cinétique chimique intervient ($i_c < i_{\mathrm{max}}$), la concentration des ions simples A à l'électrode cesse d'être négligeable, et la vague de réduction directe de ces ions est alors éventuellement observable après celle du complexe.

Jusqu'à présent, de telles courbes $\log |i_l| = f(\log \mathrm{B})$ ne paraissent pas avoir été utilisées à l'étude de complexes. Mais plusieurs travaux, surtout théoriques, ont été consacrés à la cinétique de formation des acides faibles, tels que les acides phénylglyoxalique et pyruvique plus électroactifs que les anions correspondants[1-14]. WIESNER[1], BRDIČKA[2], KOUTECKÝ[3] et DELAHAY[4] ont cherché comment la constante que nous avons désignée ici sous le nom de constante apparente de formation k_{ox} est liée aux facteurs expérimentaux.

$$k_{d_{(\mathrm{A})}} = 607\, nm^{2/3}\, t^{1/6}\, D_{\mathrm{A}}^{1/2}$$

Tout comme Ilkovic avait donné l'expression de la constante de diffusion, ces auteurs ont montré que la constante apparente de vitesse de formation est liée à la constante vraie k par la relation:

$$k_{\mathrm{ox}} = 5.3 \cdot 10^2\, nm^{2/3}\, t^{2/3}\, D_{\mathrm{A}}^{1/2} \left(\frac{k}{K}\right)^{1/2}$$

n : nombre d'électrons échangés dans la réaction d'oxydo-réduction,
m : débit du mercure en mg par sec,
t : temps de goutte en sec,
D_{A}: coefficient de diffusion de l'ion A en cm² par sec,
k : constante vraie de formation en litres par sec et par mole,
K : constante de dissociation de l'acide HA en mole par l.

Cette formule permet le calcul de la constante de formation k si la constante de dissociation K est connue — mais, d'après KOLTHOFF ET LINGANE[14], elle conduirait à des valeurs beaucoup plus grandes que celles trouvées par d'autres méthodes.

On remarque que le rapport des constantes expérimentales $\dfrac{k_{d_{(\mathrm{A})}}}{k_{\mathrm{ox}}}$, rapport qui traduit l'effet cinétique, a la valeur:

$$\frac{k_{d_{(\mathrm{A})}}}{k_{\mathrm{ox}}} = \frac{1.14\ K^{1/2}}{t^{1/2}\, k^{1/2}} \quad \ldots\ldots\ldots\ldots \quad (3)$$

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D'après cette expression, le temps de goutte est le seul facteur lié à l'appareillage susceptible de déplacer les domaines diffusion et cinétique. Mais ce temps de goutte ne peut varier que dans un domaine restreint, aussi pratiquement le rapport des constantes n'est pas modifié de plus d'un facteur 2 d'une électrode à l'autre.

B. Expression générale du courant limite—Potentiel de demi-vague

En écrivant, dans le cas général, les bilans à l'électrode de l'oxydant, du réducteur, des ions simples A et A′ et la loi d'action de masse concernant les 2 équilibres chimiques en solution, on obtient les deux expressions

$$-i_c = \triangle\,\mathrm{Ox} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$\text{et } i_a = \triangle'\,\mathrm{Red} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

où $\triangle$ et $\triangle'$, coefficients de diffusion apparents, sont donnés par les expressions:

$$\triangle = \frac{k_d \dfrac{B^b}{K_1} + k_{d(A)}\left(\dfrac{k_d}{k_A} + 1\right)}{\dfrac{B^b}{K_1} + \dfrac{k_{d(A)}}{k_A}}$$

$$\triangle' = \frac{k'_d \dfrac{B^{b'}}{K_2} + k'_{d(A')}\left(\dfrac{k'_d}{k_{A'}} + 1\right)}{\dfrac{B^{b'}}{K_2} + \dfrac{k'_{d(A')}}{k'_A}}$$

A l'aide des différentes équations, on montre que les relations suivantes, valables en l'absence de réactions chimiques, sont générales:

$$\frac{\mathrm{Ox_{el}}}{\mathrm{Ox}} = \frac{i_c - i}{i_c} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$\frac{\mathrm{Red_{el}}}{\mathrm{Red}} = \frac{i_a - i}{i_a} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

i est le courant en un point quelconque de la vague[*].

Par ailleurs, dans le cas de l'oxydo-réduction entre complexes, l'intensité i est liée au potentiel de l'électrode par la relation:

$$i = knF\,B^{(b-b')}\,\mathrm{Red_{el}}\,e^{\frac{\beta nF}{RT}E} - k'nF\,\mathrm{Ox_{el}}\,e^{\frac{-\alpha nF}{RT}E} \quad . \; . \; . \; . \quad (8)$$

En remplaçant, dans cette expression, $\mathrm{Red_{el}}$ et $\mathrm{Ox_{el}}$ par leurs valeurs tirées de (6) et (7) et en désignant par i'_e et i_e les expressions $knF\,B^{(b-b')}\,\mathrm{Red}\,e^{\frac{\beta nF}{RT}E}$ et

---

[*] Par contre, en présence de réactions chimiques, la relation entre les concentrations des corps électroactifs devient: $\triangle\,\mathrm{Ox_{el}} + \triangle'\,\mathrm{Red_{el}} = \triangle\,\mathrm{Ox_{sol}} + \triangle'\mathrm{Red_{sol}}$. Cette expression prend la forme classique $\mathrm{Ox_{el}} + \mathrm{Red_{el}} = \mathrm{Ox_{sol}} + \mathrm{Red_{sol}}$, lorsque $\triangle = \triangle'$, c'est à dire en l'absence d'effet cinétique chimique et lorsque les constantes de diffusion sont égales.

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$- k'nF$ Ox $e^{\frac{-\alpha nF}{RT}E}$ qui représentent les courants d'électrolyse que l'on observerait s'il n'y avait pas appauvrissement à l'électrode, on écrit:

$$i = i'_e \frac{i_a - i}{i_a} + i_c \frac{i_c - i}{i}$$

Si les réactions électrochimiques sont rapides, le courant i est négligeable devant l'un des termes du deuxième membre. En effet, d'une part, i est petit devant i_e et i'_e, d'autre part, l'un des rapports (6) et (7) est supérieur à 1, le premier pour un courant global d'oxydation, le deuxième pour un courant de réduction; on a donc:

soit $i \ll i'_e \dfrac{i_a - i}{i_a}$ pour un courant de réduction,

soit $i \ll i_e \dfrac{i_c - i}{i}$ pour un courant d'oxydation.

La relation (8) peut donc être simplifiée. Elle devient:

$$k \text{ Red B}^{(b-b')} \frac{i_a - i}{i_a} e^{\frac{\beta nF}{RT}E} = k' \text{Ox} \frac{i_c - i}{i_c} e^{\frac{-\alpha nF}{RT}E}$$

En posant $\alpha + \beta = 1$ dans le cas de réactions électrochimiques rapides:

$$E = \frac{RT}{nF} \log \frac{k'}{k} + \frac{RT}{nF} (b' - b) \log \text{B} + \frac{RT}{nF} \log \frac{\text{Ox}}{\text{Red}} + \frac{RT}{nF} \log \left(-\frac{i_a}{i_c}\right) + \frac{RT}{nF} \log \frac{i - i_c}{i_a - i}$$

Le terme $\dfrac{RT}{nF} \log \dfrac{k'}{k}$ est le potentiel normal apparent $E_\circ'$ du couple oxydo-réducteur à la force ionique considérée.

L'expression générale du potentiel de demi-vague est donc

$$E_{1/2} = E_\circ' + \frac{RT}{nF} (b' - b) \log \text{B} + \frac{RT}{nF} \log \frac{\text{Ox}}{\text{Red}} + \frac{RT}{nF} \log \left(-\frac{i_a}{i_c}\right) \quad . \; . \; . \quad (9)$$

ou, en explicitant Ox et Red:

$$\boxed{E_{1/2} = E_\circ' + \frac{RT}{nF} \log \frac{\text{B}^{b'} + K_2}{\text{B}^{b} + K_1} + \frac{RT}{nF} \log \left(-\frac{i_a}{i_c} \times \frac{c}{c'}\right)} \quad . \; . \; . \quad (10)$$

Le potentiel de demi-vague ne parait dépendre que du degré de formation des complexes, mais les courants limites font intervenir implicitement les facteurs cinétiques.

En remplaçant i_a et i_c par leurs valeurs tirées de (4) et (5) on peut aussi écrire:

$$E_{1/2} = E_\circ' + \frac{RT}{nF} (b' - b) \log \text{B} + \frac{RT}{nF} \log \frac{\triangle}{\triangle'} \quad . \; . \; . \; . \; . \quad (11)$$

Au potentiel de demi-vague, d'après (6) et (7), les concentrations Ox_{el} et Red_{el} ne sont égales que si $\triangle = \triangle'$ ce qui implique l'absence d'effet cinétique chimique. En effet, dans le cas général, $Ox_{el} = Red_{el}$ pour un potentiel différent de $E_{1/2}$ défini par:

$$i = \frac{\triangle i_c + \triangle' i_a}{\triangle + \triangle'}$$

L'expression (10) se simplifie:

(a) Lorsque les complexes sont quantitativement formés:

$$E_{1/2} = E_{\circ}' + \frac{RT}{nF}(b-b') \log \mathrm{B},$$

si les deux constantes de diffusion de Ox et de Red sont égales, d'où $E_{\circ}'$ et $b'-b$.

La cinétique n'intervient pas.

(b) Lorsque les complexes ne sont pratiquement pas formés, s'il subsiste une vague:

$$E_{1/2} = E_{\circ}' + \frac{RT}{nF} \log \frac{K_2}{K_1} + \frac{RT}{nF} \log \left(-\frac{i_a}{i_c} \times \frac{c}{c'}\right)$$

La courbe $E_{1/2} = f\left[\log\left(-\frac{i_a}{i_c} \times \frac{c}{c'}\right)\right]$ est alors une droite indépendante de B, qui permet d'atteindre l'expression: $E_{\circ}' + \frac{RT}{nF} \log \frac{K_2}{K_1} = E_{\circ}''$ potentiel normal apparent du couple des ions simples et le rapport $\frac{K_2}{K_1}$ si $E_{\circ}'$ est connu par ailleurs.

II. LES IONS SIMPLES SONT PLUS ÉLECTROACTIFS QUE LES COMPLEXES

Réactions à l'électrode dans le domaine de potentiel considéré: $\underset{\text{Ox}}{\mathrm{A}} + ne \rightleftarrows \underset{\text{Red}}{\mathrm{A'}}$

En écrivant comme précédemment, les bilans à l'électrode, on montre que les relations (6) et (7) sont toujours valables et que le potentiel de demi-vague est donné par la formule générale:

$$E_{1/2} = E_{\circ}'' + \frac{RT}{nF} \log \frac{\text{Ox}}{\text{Red}} \quad \frac{RT}{nF} \log \left(-\frac{i_a}{i_c}\right)$$

$$\text{ou } E_{1/2} = E_{\circ}'' + \frac{RT}{nF} \log \frac{K_1}{K_2} + \frac{RT}{nF} \log \frac{\mathrm{B}^{b'} + K_2}{\mathrm{B}^{b} + K_1} + \frac{RT}{nF} \log \left(-\frac{i_a}{i_c} \times \frac{c}{c'}\right)$$

$E_{\circ}''$, potentiel normal apparent du couple des ions simples; on retrouve l'expression (10) si on remarque que $E_{\circ}'' + \frac{RT}{nF} \log \frac{K_1}{K_2} = E_{\circ}'$, potentiel normal apparent du couple des complexes, inaccessible directement dans le cas présent.

Considérons toujours l'exemple du courant limite cathodique dont l'expression générale est:

$$-i_c = k_d \text{Ox} + k_{\text{ox}} \text{AB}_{\text{el}}^{b}$$

dans laquelle le deuxième terme représente la vitesse de dissociation du complexe

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à l'électrode ou la vitesse de formation chimique de Ox, égale par ailleurs à la vitesse de diffusion du complexe:

$$k_{\mathrm{Ox}}\,\mathrm{AB}^b_{\mathrm{el}} = k_{d(\mathrm{AB}^b)}\,(\mathrm{AB}^b - \mathrm{AB}^b_{\mathrm{el}})$$

Le rapport des vitesses maxima de ces deux phénomènes:

$\dfrac{k_{\mathrm{Ox}}\ \mathrm{AB}^b}{k_{d(\mathrm{AB}^b)}\,\mathrm{AB}^b} = \dfrac{k_{\mathrm{Ox}}}{k_{d(\mathrm{AB}^b)}}$, indépendant de B, est déterminé pour un système et un dispositif expérimental donnés. Soit les deux cas simples:

1. *Mise en équilibre rapide des complexes devant leur diffusion*

On a alors: $k_{\mathrm{Ox}} \gg k_{d(\mathrm{AB}^b)}$ et $\mathrm{AB}^b_{\mathrm{el}} \ll \mathrm{AB}^b$

$$-i_c = k_d\,\mathrm{Ox} + k_{d(\mathrm{AB}^b)}\ \mathrm{AB}^b$$

$$i_c = i_{\max(\mathrm{ox})} \text{ si la réaction chimique est nulle.}$$

$$i_c = i_{\max(\mathrm{AB}^b)} \text{ si la réaction chimique est quantitative.}$$

Si les constantes de diffusion sont égales:

$$-i_c = k_d c = -i_{\max}$$

Le courant limite est constant, quel que soit le degré de formation des complexes, c'est à dire B. Il ne donne donc aucun renseignement sur les complexes.

Le potentiel de demi-vague varie tant que les réactions chimiques ne sont pas nulles.

Lorsque les réactions sont quantitatives, si les constantes de diffusion de Ox et de Red sont égales:

$$E_{1/2} = \underbrace{E_\circ'' + \frac{RT}{nF}\log\frac{K_1}{K_2}}_{E_\circ'} + \frac{RT}{nF}\log\,(b'-b)\log \mathrm{B}$$

d'où $b'-b$, $\mathrm{E}_\circ'$ potentiel normal apparent du couple des complexes, et $\dfrac{K_1}{K_2}$ si $E_\circ''$ est déterminé par ailleurs en l'absence d'ions complexants.

C'est le cas le plus fréquemment étudié par polarographie.

2. *Mise en équilibre lente des complexes devant leur diffusion* (Fig. 2)

$k_{d(\mathrm{AB}^b)} \gg k_{\mathrm{Ox}}$, le complexe ne diffuse pratiquement pas.

$$\mathrm{AB}^b_{\mathrm{el}} \backcong \mathrm{AB}^b$$

$$\text{et}\quad -i_c = k_d\,\mathrm{Ox} + k_{\mathrm{Ox}}\,\mathrm{AB}^b$$

suivant la concentration de l'ion complexant B, l'un des deux termes peut être négligeable devant l'autre, d'où deux domaines extrêmes à considérer, concernant cette fois l'ion actif:

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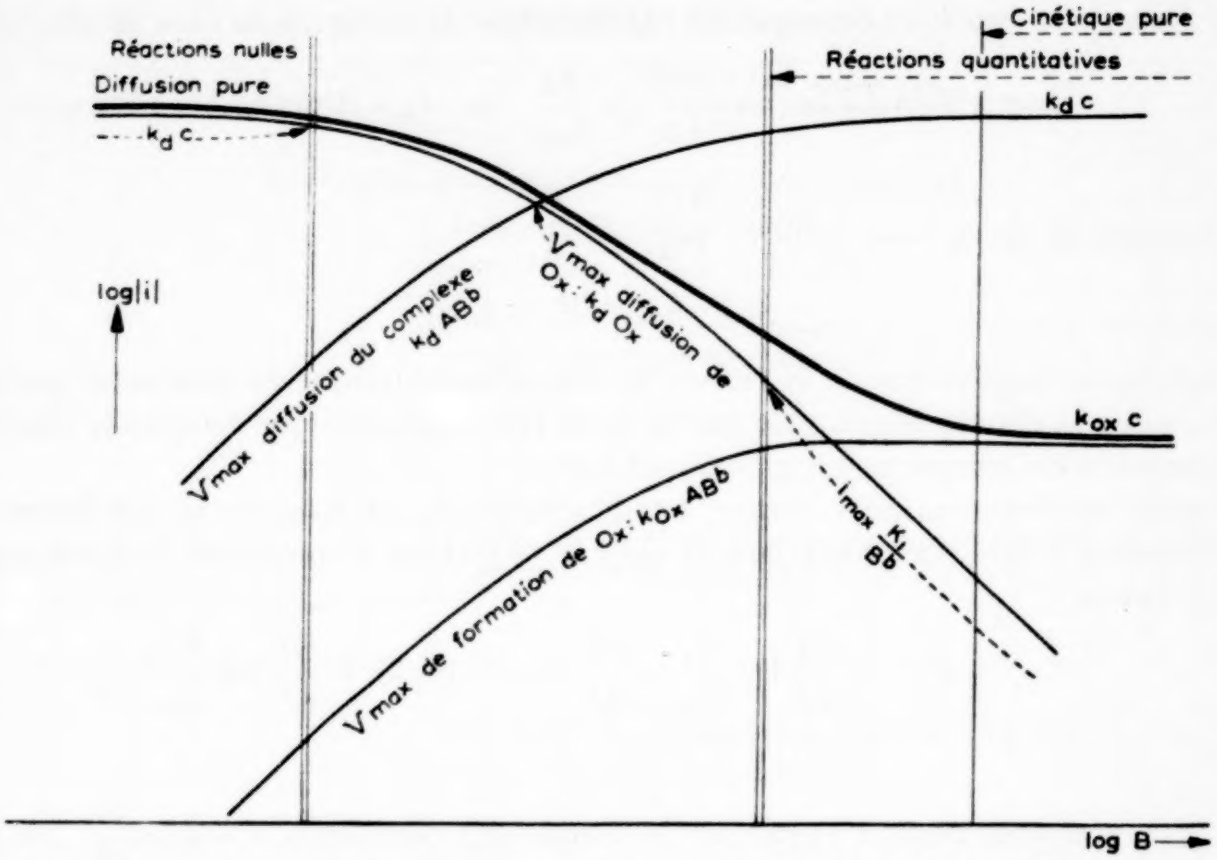

Fig. 2. Ions simples électroactifs. ——— = variation de l'intensité limite cathodique en fonction de la concentration de l'ion complexant lorsque les réactions chimiques sont lentes devant la diffusion des complexes. ($k_{\text{Ox}} \ll k_d$). On suppose $k_d = k_{d(\mathrm{AB}^b)}$.
Ox = ion simple actif; AB^b = complexe inactif; k_{ox} = constante apparente de formation de l'ion simple actif.

(a) *La mise en équilibre chimique est lente devant la diffusion de l'ion simple actif:*

$$k_{\text{ox}}\,\mathrm{AB}^b \ll k_d\mathrm{Ox} \quad \text{ou} \quad \frac{\mathrm{AB}^b}{\mathrm{Ox}} \ll \frac{k_d}{k_{\text{ox}}}$$

$$\downarrow$$

$$\frac{\mathrm{B}^b}{K_1} \qquad \text{soit } k_{\mathrm{AB}^b}\,\mathrm{B}^b \ll k_d \text{ puisque } \frac{k_{\text{ox}}}{k_{\mathrm{AB}^b}} = K_1$$

$$-\,i_c = k_d\mathrm{Ox} = k_d\,\frac{c}{1 + \dfrac{\mathrm{B}^b}{K_1}} = -\,i_{\max}\,\frac{1}{1 + \dfrac{\mathrm{B}^b}{K_1}}$$

seule, la diffusion des ions actifs limite le courant (portion de gauche de la courbe Fig. 2).
Lorsque la réaction chimique est nulle $i_c = i_{\max}$.
Excepté dans ce dernier cas, la constante de dissociation du complexe peut être déterminée.

Si la condition (a) est réalisée à la fois pour l'oxydant et pour le réducteur, et si les constantes de diffusion de Ox et de Red sont égales, le potentiel de demi-vague est constant et égal à E_0'', quel que soit le degré de formation des complexes.

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(b) *La mise en équilibre chimique est rapide devant la diffusion de l'ion simple actif*:

$$k_{\mathrm{Ox}}\,\mathrm{AB}^b \gg k_d\mathrm{Ox} \quad \text{ou} \quad \frac{\mathrm{AB}^b}{\mathrm{Ox}} \gg \frac{k_d}{k_{\mathrm{Ox}}} \quad \text{ou} \quad k_{\mathrm{AB}^b}\,\mathrm{B}^b \gg k_d$$

$$\text{donc} \quad \frac{\mathrm{AB}^b}{\mathrm{Ox}} \quad \text{ou} \quad \frac{\mathrm{B}^b}{K_1} \gg 1$$

$$-i_c = k_{\mathrm{Ox}}\,\mathrm{AB}^b = k_{\mathrm{Ox}}c$$

Le courant ne dépend que de la vitesse de formation chimique de l'ion actif (portion de droite de la courbe Fig. 2). Ce cas ne peut être rencontré que lorsque la réaction de formation du complexe est très quantitative.

D'après les deux courants limites, on détermine k_{Ox} et k_{red}. Si la condition (b) est remplie à la fois pour l'oxydant et pour le réducteur, le potentiel de demi-vague a pour valeur:

$$E_{1/2} = \underbrace{E_\circ'' + \frac{RT}{nF}\log\frac{K_1}{K_2}}_{E_\circ'} + \frac{RT}{nF}(b'-b)\log\mathrm{B} + \frac{RT}{nF}\log\frac{k_{\mathrm{red}}}{k_{\mathrm{Ox}}}$$

d'où $E_\circ'$, potentiel normal apparent du couple des complexes, $b'-b$, et $\frac{K_1}{K_2}$, si $E_\circ''$ est déterminé par ailleurs en l'absence d'ions complexants.

Remarque

Dans le cas de la Fig. 2 où la cinétique chimique est suffisamment lente ($k_{\mathrm{Ox}} \ll k_{d_{(\mathrm{AB}^b)}}$), la vague de réduction directe du complexe est éventuellement observable après celle des ions simples, à condition que le complexe soit suffisamment formé.

Après avoir écrit les relations concernant l'oxydo-réduction des ions simples en présence d'ions complexants, nous avons eu connaissance d'un travail récent de STROMBERG[15] qui a calculé les expressions des courants limites et du potentiel de demi-vague dans le cas suivant: oxydo-réduction cation métallique/amalgame — le cation étant susceptible de former un complexe inactif. Les formules données sont analogues aux précédentes où il faut alors supprimer les termes relatifs à la réaction chimique du réducteur.

CONCLUSION

Dans le Tableau I, sont rassemblés quelques uns des résultats précédents, obtenus d'une part dans le cas des complexes, d'autre part dans le cas des ions simples actifs. La comparaison est réduite aux deux cas extrêmes où les réactions chimiques de formation des complexes sont quantitatives ou nulles. De plus, pour simplifier, nous avons supposé que les différents domaines coincident pour l'oxydant et le réducteur, ce qui est tout à fait arbitraire, et nous avons confondu toutes les constantes de diffusion k_d ainsi que les deux concentrations c et c'.

On voit d'abord que l'influence de la cinétique chimique permet de déterminer la nature de la réaction électrochimique à l'électrode. En effet, lorsque les réactions chimiques sont très rapides, il n'est pas possible de préciser le mécanisme des réactions dans un mélange d'ions simples et de complexes. Dans les deux cas $i_l = i_{\max}$ et les

TABLEAU I

Complexes actifs *(Potentiel normal apparent $E_\circ'$)*	*Ions simples actifs* *(Potentiel normal apparent $E_\circ''$)*
RÉACTIONS QUANTITATIVES (COMPLEXES FORMÉS)	
	I. Mise en équilibre chimique lente devant la diffussion des complexes (k_{ox} *et* $k_{red} \ll k_d$; Fig. 2) (a) Mise en équilibre chimique lente devant la diffusion des ions actifs ($k_{AB^b}\,B^b$ *et* $k_{AB^{b'}}\,B^{b'} \ll k_d$) $i_c = i_{max}\,\frac{K_1}{B^b}$; $i_a = i_{max}\,\frac{K_2}{B^{b'}}$ $E_{1/2} = E_\circ''$
$i_c = i_{max}\quad i_a = i_{max}$ $E_{1/2} = E_\circ' + \frac{RT}{nF}(b'-b)\log B$	(b) Mise en équilibre chimique rapide devant la diffusion des ions actifs ($k_{AB^b}\,B^b$ *et* $k_{AB^{b'}}\,B^b \gg k_d$) $-i_c = k_{ox}c$; $i_a = k_{red}c$ $E_{1/2} = \underbrace{E_\circ'' + \frac{RT}{nF}\log\frac{K_1}{K_2}}_{E_\circ''} + \frac{RT}{nF}(b'-b)\log B + \frac{RT}{nF}\log\frac{k_{red}}{k_{ox}}$
	II. Mise en équilibre chimique rapide devant la diffusion des complexes (k_{ox} *et* $k_{red} \gg k_d$) $i_c = i_{max}$; $i_a = i_{max}$ $E_{1/2} = \underbrace{E_\circ'' + \frac{RT}{nF}\log\frac{K_1}{K_2}}_{E_\circ'} + \frac{RT}{nF}(b'-b)\log B$
RÉACTIONS NULLES (COMPLEXES NON FORMÉS)	
I. Mise en équilibre chimique lente devant la diffusion des complexes (k_A *et* $k_A' \ll k_d$) $i_c = i_{max}\,\frac{B^b}{K_1}$; $i_a = i_{max}\,\frac{B^{b'}}{K_2}$ $E_{1/2} = E_\circ' + \frac{RT}{nF}(b'-b)\log B$	
II. Mise en équilibre chimique rapide devant la diffusion des complexes (k_A *et* $k_A' \gg k_d$; Fig. 1.) (a) Mise en équilibre chimique rapide devant la diffusion des ions simples ($k_{ox}B^b$ *et* $k_{red}B^{b'} \gg k_d$) $i_c = i_{max}$; $i_a = i_{max}$ $E_{1/2} = E_\circ' + \frac{RT}{nF}\log\frac{K_2}{K_1} = E_\circ''$	$i_c = i_{max}$; $i_a = i_{max}$ $E_{1/2} = E_\circ''$
(b) Mise en équilibre chimique lente devant la diffusion des ions simples ($k_{ox}B^b$ *et* $k_{red}B^{b'} \ll k_d$) $-i_c = k_{ox}B^b c\qquad i_a = k_{red}B^{b'}c$ $E_{1/2} = \underbrace{E_\circ' + \frac{RT}{nF}\log\frac{K_2}{K_1}}_{E_\circ''} + \frac{RT}{nF}(b'-b)\log B + \frac{RT}{nF}\log\frac{k_{red}}{k_{ox}}$	

potentiels de demi-vague ont les mêmes valeurs. Mais, lorsque les réactions chimiques sont assez lentes, on observe une variation de l'intensité limite avec la concentration de l'ion complexant; si cette intensité diminue quand (B) augmente, on peut conclure à l'activité électrochimique de l'ion simple. Si au contraire elle diminue en même temps que (B), c'est le complexe qui agit à l'électrode.

Si de plus, l'intensité limite est supérieure à ce qu'elle serait si l'espèce active était amenée à l'électrode uniquement par diffusion, les constantes de vitesse interviennent et les deux conditions suivantes se trouvent à la fois satisfaites: les mises en équilibre chimiques sont rapides devant la diffusion de l'espèce active mais elles sont lentes devant la diffusion du corps qui donne chimiquement naissance à cette espèce active.

Par ailleurs, pour que les constantes de dissociation K_1 et K_2 figurent dans les expressions de i_l et de $E_{1/2}$, il faut que la concentration des corps électroactifs varie avec (B). L'effet est maximum lorsque la formation du corps électroactif est pratiquement nulle.

ÉTUDE EXPÉRIMENTALE DE L'ÉLECTROACTIVITÉ DU COUPLE Ti(IV)/Ti(III) EN PRÉSENCE D'IONS THIOCYANATES

Potentiel normal apparent des couples $TiOH^{+3}/Ti^{+3}$ et $TiOH{\cdot}SCN^{+2}/TiSCN^{+2}$

Nous donnons seulement un résumé des résultats qui seront exposés par ailleurs de façon plus détaillée[16].

En milieu perchlorique ou chlorhydrique, les réactions électrochimiques Ti(IV) + e $\rightleftarrows$ Ti(III) sont lentes à l'électrode à gouttes de mercure.

Mais les réactions deviennent rapides en présence d'ions thiocyanates.

A. Solutions chlorhydriques de titane(IV) et de titane(III) en présence de thiocyanate

Les vagues cathodique et anodique sont toutes les deux observables; leurs potentiels de demi-vague ont la même valeur.

Avec la concentration de l'ion complexant, les deux intensités limites varient comme sur la Fig. 1; la réaction électrochimique rapide met donc en jeu deux complexes thiocyanés du titane dont les vitesses de mise en équilibre chimique interviennent lorsque la concentration de l'ion complexant est assez faible.

Dans ce domaine, nous avons déterminé b et b' en étudiant les deux fonctions simples:

$$\frac{i_c}{i_{\max}-i_c} = \frac{k_{\text{ox}}}{k_d}\,\mathrm{B}^b \quad \text{et} \quad \frac{i_a}{i_{\max}-i_a} = \frac{k_{\text{red}}}{k_d}\,\mathrm{B}^{b'}$$

Les courbes représentatives en fonction de (SCN^-) sont des droites donc $b = b' = 1$.

Les constantes de diffusion des différentes espèces mises en jeu ont sensiblement la même valeur.

Par ailleurs, l'étude du potentiel de demi-vague en fonction du pH a montré que la réduction électrochimique consomme un ion H^+.

D'après l'ensemble de ces résultats, la réaction à l'électrode doit être écrite:

$$TiOH{\cdot}SCN^{+2} + H^+ + e \rightleftarrows TiSCN^{+2} + H_2O$$

La formule du complexe thiocyané du titane(IV), $TiOH{\cdot}SCN^{+2}$, a été vérifiée par d'autres méthodes[16–18].

Les deux complexes sont très peu stables; il n'a pas été possible d'atteindre le domaine des réactions quantitatives, donc de déterminer directement le potentiel normal apparent $E_\circ'$ du couple des complexes.

Nous avons tracé la courbe $E_{1/2} = f\left[\log\left(-\frac{i_a}{i_c} \times \frac{c}{c'}\right)\right]$ pour les différentes concentrations de thiocyanate (Fig. 3), les valeurs de $E_{1/2}$ étant ramenées à pH 0 [(H^+) expérimental = 0.55M]. D'après la formule générale (10) (p. 80), cette courbe tend vers une droite de pente 0.06 lorsque la formation des deux complexes est pratiquement nulle. L'extrapolation de la partie linéaire pour $-\frac{i_a}{i_c} \times \frac{c}{c'} = 1$ donne la valeur de l'expression:

$E_\circ' + 0.06 \log \frac{K_2}{K_1} = -0.30 + 0.01$ V (E.C.S.) $= E_\circ''$, potentiel normal apparent, à force ionique 0.5, du couple des ions simples $TiOH^{+3}/Ti^{+3}$. Cette grandeur caractéristique ne peut pas être déterminée directement à partir des ions simples du titane car les réactions électrochimiques correspondantes sont trop lentes.

$$E_\circ'' = -0.055 \pm 0.01 \text{ V (E.N.H.)}, \mu = 0.5$$

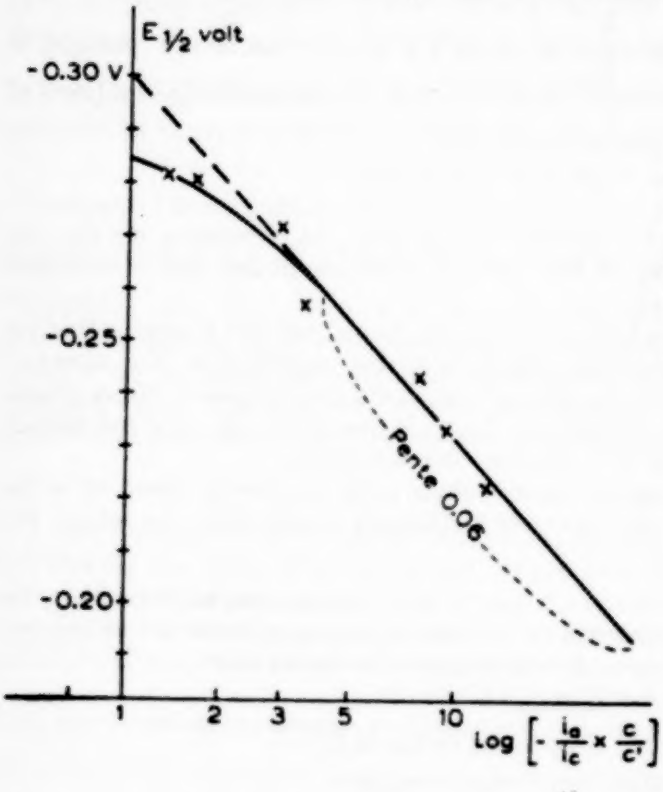

Fig. 3. Détermination de $E_\circ' + 0.06 \log \frac{K_2}{K_1} = E_\circ''$ potentiel normal apparent du couple des ions simples $TiOH^{+3}/Ti^{+3}$ d'après l'extrapolation de la partie linéaire de la courbe $E_{1/2} = f\left[\log\left(-\frac{i_a}{i_c} \times \frac{c}{c'}\right)\right]$ pour $-\frac{i_a}{i_c} \times \frac{c}{c'} = 1$.

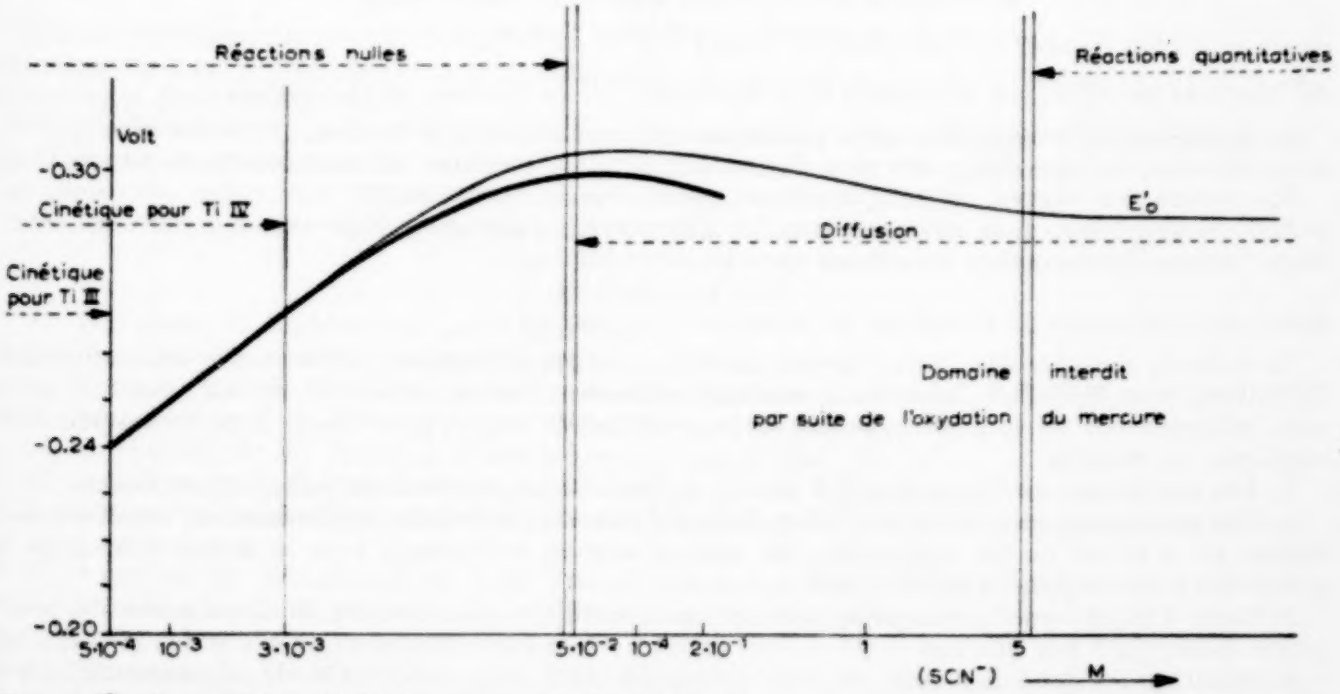

Fig. 4. Étude expérimentale du potentiel de demi-vague. ——— = courbe calculée au moyen des constantes déterminées expérimentalement, d'après l'expression:

$$E_{1/2(\text{calc.})} = E_\circ' + 0.06 \log (H^+) + 0.06 \log \frac{K_2 + SCN^-}{K_1 + SCN^-} + 0.06 \log \frac{SCN^- + \frac{k_d}{k_{ox}}}{SCN^- + \frac{k_d}{k_{red}}} = f(\log SCN^-).$$

——— = courbe expérimentale. $E_{1/2} = f(\log SCN^-)$ pour $[H^+] = 0.55M$.

La valeur expérimentale de $E_\circ''$ permet le calcul de $E_\circ'$ potentiel normal apparent du couple des complexes, si le rapport $\frac{K_2}{K_1}$ est connu. Théoriquement, les deux constantes K_1 et K_2 sont calculables d'après la formule (10) lorsque la formation chimique des complexes cesse d'être nulle. Dans le cas présent, ceci se produit seulement à l'extrémité du domaine étudié, lorsque la concentration du thiocyanate devient de l'ordre de $10^{-1}M$, mais les variations de $E_{1/2}$ sont alors très faibles (courbe expérimentale $E_{1/2} = f(\log \text{SCN}^-)$, Fig. 4) – ceci parce que les constantes K_1 et K_2 ont des valeurs voisines. Par ailleurs, l'oxydation du mercure de l'électrode empêche la détermination du potentiel de demi-vague, lorsque la concentration du thiocyanate dépasse $2.10^{-1}M$.

Les valeurs des constantes K_1 et K_2 ont été obtenues par spectrophotométrie, $K_1 = 0.8 \pm 0.2$, $K_2 = 0.33 \pm 0.05$[16,17]. En adoptant pour le rapport $\frac{K_1}{K_2}$ la valeur 2.5 ± 1, nous avons calculé le potentiel normal apparent du couple des complexes $\text{TiOH·SCN}^{+2}/\text{TiSCN}^{+2}$ à pH 0 et force ionique 0.5:

$$E_\circ' = -0.275 \pm 0.020 \text{ V (E.C.S.)}$$
$$\text{soit } E_\circ' = -0.03 \pm 0.02 \text{ V (E.N.H.)}, \mu = 0.5$$

Oxydation chimique parasite Sur la Fig. 4 sont portées—d'une part, la variation de $E_{1/2}$ en fonction de (SCN^-) que l'on devrait observer d'après les valeurs expérimentales des différentes constantes — d'autre part, la courbe expérimentale.

Ces deux courbes coincident dans le domaine étudié à 0.01 V près, ce qui justifie l'interprétation donnée aux phénomènes, et en particulier les valeurs des différentes constantes. On observe cependant un léger écart qui tend à augmenter avec la concentration du thiocyanate. Nous avons vérifié que cet écart est lié à la présence de traces d'oxydant. Dans le cas de la Fig. 4, il est réduit au minimum, 0.01 V, par une élimination soignée de l'oxygène des solutions.

Mais la courbe expérimentale du potentiel de demi-vague s'éloigne de la courbe calculée si les courbes cathodiques sont tracées en présence d'une quantité suffisante d'oxydant: oxygène, fer ferrique, grand excès d'ions ClO_4^- etc.

Coefficient de diffusion et constantes de vitesse vraies. A partir des valeurs de la constante de diffusion expérimentale k_d et des constantes apparentes de vitesse k_{ox} et k_{red} nous avons calculé le coefficient de diffusion de la relation d'Ilkovic pour les différents ions du titane:

$$D = 6 \pm 0.5 \cdot 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$$

et les constantes vraies de vitesse de formation à 21° d'après la relation (3):

$$k_{(\text{formation de TiOH·SCN}^{+2})} = 6 \pm 2 \cdot 10^3 \text{ l} \cdot \text{sec}^{-1} \cdot \text{mole}^{-1}$$
$$k_{(\text{formation de TiSCN}^{+2})} \sim 10^6 \text{ l} \cdot \text{sec}^{-1} \cdot \text{mole}^{-1}$$

B. Solutions perchloriques de titane(IV) et de titane(III) en présence de thiocyanate

En milieu perchlorique, la vague anodique est généralement perturbée, d'autant plus que la concentration des ions ClO_4^- est plus élevée; ces derniers oxydent chimiquement le titane(III).

Par contre, les vagues cathodiques de solutions diluées de titane(IV) sont celles observées en milieu chlorhydrique si la concentration des ions perchloriques reste inférieure à $0.5M$; les réactions électrochimiques sont les mêmes dans les deux milieux.

Remarque concernant les complexes du titane avec les ions Cl^-

En milieu chlorhydrique, nous n'avons pas tenu compte de l'existence éventuelle des complexes $\text{Ti}^{\text{IV}}\text{OH·Cl}^{+2}$ et $\text{Ti}^{\text{III}}\text{Cl}^{+2}$. En effet, la concentration du chlorure, entre 0.1 et $1M$, nous a paru sans influence sur les intensités limites et le potentiel de demi-vague. Deux hypothèses peuvent expliquer ce résultat:

1. Les complexes du titane avec Cl^- sont trop peu stables pour exister dans ces conditions.
2. Les deux complexes $\text{Ti}^{\text{IV}}\text{OH·Cl}^{+2}$ et $\text{Ti}^{\text{III}}\text{Cl}^{+2}$ ont des constantes de dissociation sensiblement égales, et, à partir de ces complexes, les espèces actives se forment avec la même vitesse qu'à partir des ions simples TiOH^{+3} et Ti^{+3}.

A l'aide d'équilibres d'extraction, nous avons montré que la constante de dissociation du complexe TiOH·Cl^{+2} est environ 0.5[18]. L'ion TiOH·Cl^{+2} existe donc peu pour Cl^- $0.1M$ mais sa concentration est deux fois celle de l'ion simple TiOH^{+3} lorsque Cl^- $1M$. Il conviendrait donc de retenir la deuxième hypothèse. Il reste à montrer que la constante de dissociation du complexe $\text{Ti}^{\text{III}}\text{Cl}^{+2}$ est, elle aussi, voisine de 0.5.

Application à la chimie analytique

La vague polarographique due à l'oxydo-réduction rapide des complexes monothiocyanés peu stables du titane permet le dosage de l'élément. Ce dosage est possible,

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— *même lorsque les complexes actifs existent en faible proportion par rapport aux ions simples* — parce que les réactions chimiques sont suffisamment rapides. Il faut choisir une concentration assez élevée en thiocyanate pour que la valeur du courant mesuré soit d'une part maximum, et — d'autre part, peu sensible à une légère variation de la quantité d'agent complexant libre.

Dans certains cas, une partie du thiocyanate peut être consommée par des ions étrangers, ce qui perturbe les résultats si la diminution de SCN^- libre est assez grande pour que le courant limite du titane ne soit plus contrôlé uniquement par la diffusion. Le tracé des courbes d'étalonnage $i_{l(Ti)} = f(SCN^-)_{total}$ en présence d'ions gênants permet alors de contrôler l'influence de ces ions et de fixer ensuite en conséquence la concentration totale du thiocyanate convenant aux dosages.

Exemple: Dosage du titane(IV) en présence de fer(III). En présence de thiocyanate $10^{-1}M$ et de gélatine (7 mg %), le titane(IV) est dosable pour un rapport moléculaire $\frac{Fe(III)}{Ti(IV)} \leqslant 25$ avec $Fe(III) \leqslant 5 \cdot 10^{-3}M$ — ceci en milieu acide normal. La vague du fer(III) précède celle du titane(IV), mais ne gêne pas la détermination de l'intensité limite de cette dernière. Il n'y a pas lieu de tenir compte de la consommation du thiocyanate par le fer(III) dans les conditions indiquées. La concentration tolérable en fer(III) est limitée à $5 \cdot 10^{-3}M$, car pour de plus fortes teneurs, des maxima apparaissent sur les courbes polarographiques.

RÉSUMÉ

L'oxydo-réduction électrochimique du couple titane(IV) – titane(III) est lente à l'électrode à gouttes de mercure en milieu perchlorique ou chlorhydrique, mais elle devient rapide en présence d'ions thiocyaniques.

A l'aide des courbes de polarisation, interprétées d'après une étude théorique préliminaire, nous avons conclu que la réaction électrochimique rapide est la suivante:

$$TiOH{\cdot}SCN^{+2} + H^+ + e \rightleftarrows TiSCN^{+2} + H_2O$$

Une application au dosage polarographique du titane est donnée.

SUMMARY

The electrochemical oxidation-reduction of the system titanium(IV) – titanium(III) is slow at dropping mercury electrode in perchloric acid or hydrochloric acid, but becomes rapid in the presence of thiocyanate ions.

On the basis of polarization curves, interpreted according to a preliminary theoretical study, the authors conclude that the rapid electrochemical reaction is the following:

$$TiOH{\cdot}SCN^{+2} + H^+ + e \rightleftarrows TiSCN^{+2} + H_2O$$

An application of the findings to the polarographic determination of titanium is given.

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Reçu le 14 octobre 1957

NITRATION ET DOSAGE DE LA PHÉNYLALANINE

par

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INTRODUCTION

La première méthode analytique employée pour la détermination de la phénylalanine est due à KOLLMANN[1] dont le procédé est basé sur l'oxydation de cette substance par le dichromate de potassium en milieu sulfurique. L'acide benzoïque formé est extrait à l'éther, séché et pesé. Elle ne convient que pour des quantités importantes de phénylalanine. En 1930, BRAZIER[2] introduit une méthode de dosage d'une série d'acides aminés basée sur la différence de solubilité de leurs sels cuivriques dans divers solvants. Plus récemment, plusieurs méthodes chromatographiques ont été mises au point principalement par MARTIN ET SYNGE[3]. KAPELLER-ADLER[4] propose une méthode colorimétrique par nitration de la phénylalanine et développement d'une coloration violette par l'hydroxylamine. Le mécanisme de cette réaction a été étudié par BLOCK ET BOLLING[5], grâce à une modification, ils dosent jusqu'à 0.5 mg de substance. La précision n'est pas donnée. HESS ET SULLIVAN[6] déterminent la phénylalanine dans un hydrolysat de protéines par oxydation préalable au permanganate pour détruire la tyrosine puis nitration par un mélange acide sulfurique concentré-nitrate de potassium. La coloration est développée par le naphtoquinone sulfonate de potassium. La mesure se fait à 540 mμ. MONNIER ET RUSCONI ont proposé[7] une méthode de dosage polarographique après nitration de la phénylalanine. Cette étude a été reprise et les conditions de nitration systématiquement examinées afin de rendre le dosage aussi précis, sensible et spécifique que possible.

Au cours de ce travail, toutes les courbes ont été obtenues au moyen du polarographe Sargent XXI et l'électrode à gouttes de mercure. L'hydrogène intervenant dans la réduction polarographique, les solutions ont été tamponnées.

pH	*Ac. citrique 0.1M*	*Phosphate disodique 0.2M*
2.2	19.6 ml	0.4 ml
3	15.9	4.1
4	12.29	7.71
5	9.7	10.3
6	7.37	12.63
7	3.53	16.47
8	0.55	19.45

I. ÉTUDE DE LA NITRATION DE LA PHÉNYLALANINE

Conditions de nitration de la phénylalanine

Les nitrations sont effectuées à l'ébullition pendant 1 h par chauffage à reflux avec HNO_3 à diverses concentrations et le mélange H_2SO_4 conc.-KNO_3. Le produit de nitration est dilué, neutralisé avec KOH en présence de rouge de méthyle (qui sert d'indicateur et de „suppresseur" de maximum), additionné de 10 ml de tampon, amené au volume de 50 ml et polarographié après avoir enlevé l'oxygène dissous par un courant d'hydrogène. Les résultats sont donnés dans le Tableau I.

TABLEAU I

Concentration HNO_3	*Concentration phénylalanine*		$i_d (\mu A)$	$K (i_d/c)$
	g/l	*M*		
3.3*N* 4.5*N*	pas de sauts, nitration nulle			
6.7*N*	0.12	$0.73 \cdot 10^{-3}$	3.3	4.5
	0.17	1.03	4.4	4.3
	0.22	1.30	6.6	5.0
8.3*N*	0.23	1.39	15.0	10.8
	0.18	1.09	12.3	11.2
10*N*	0.14	0.85	8.6	10.2
	0.28	1.70	19.7	11.6
	0.20	1.21	14.3	11.7
11.5*N*	0.18	1.10	14.0	12.6
	0.28	1.70	22.7	13.2
	0.14	0.05	10.7	12.5
13.5*N*	0.23	1.40	20.1	14.4
	0.18	1.09	16.4	15.0
H_2SO_4-KNO_3	0.12	0.73	16.7	23.0
	0.18	1.09	26.9	25.0
	0.14	0.85	20.8	24.5

L'examen du Tableau I montre que pour la concentration en $HNO_3 \leqslant 4.5N$, il n'y a pas de nitration. Entre 6.7*N* et 8.3*N*, on observe une grande différence dans la hauteur des sauts qui est, par contre, à peu près constante de 8.3 à 10*N*.

Le mélange H_2SO_4 conc.-KNO_3 donne des sauts beaucoup plus grands car la nitration est plus poussée, mais les vagues sont moins bien dessinées et les sauts plus difficiles à mesurer.

Nous avons fait varier la durée de la nitration entre 45 min et 2 h, les courbes polarographiques sont très semblables particulièrement entre 1 et 2 h.

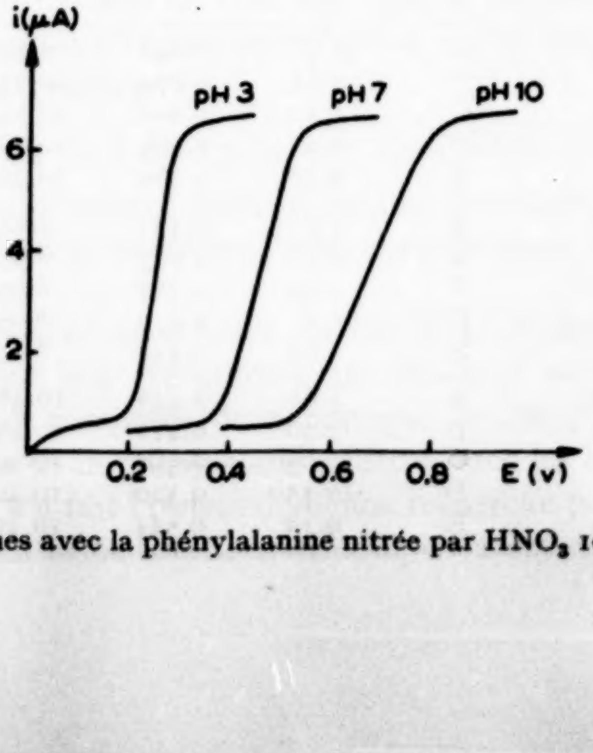

Fig. 1. Courbes obtenues avec la phénylalanine nitrée par HNO_3 10*N*. $C = 0.5 \cdot 10^{-3} M$.

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Étude des courbes polarographiques de solutions de phénylalanine nitrée par HNO_3 10N

En fonction du pH. Pour ces essais, 43.6 mg de phénylalanine ont été traités pendant $1\frac{1}{2}$ h avec HNO_3 10N, neutralisés; puis le volume a été porté à 100 ml. Des parties aliquotes de 10 ml ont été prélevées et portées à 50 ml par un tampon approprié (voir p. 90). Les potentiels $E_{\frac{1}{2}}$ sont donnés par rapport à l'électrode au calomel saturé (Tableau II).

TABLEAU II

ÉTUDE EN FONCTION DU pH, AVEC ÉLECTRODE DE RÉFÉRENCE AU CALOMEL

concentration phénylalanine $0.62 \cdot 10^{-3} M$

pH	$i\ (\mu A)$	$E_{1/2}\ (V)$	$\Delta E_{1/2}/\Delta pH$
2.8	6.3	0.235	0.070
3.8	6.2	0.305	0.050
4.9	6.2	0.360	0.054
6.0	6.4	0.420	0.030
7.0	6.2	0.450	0.066
8.5	6.15	0.550	0.047
10.0	6.1	0.620	0.045
10.9	6.15	0.660	0.050
11.7	6.1	0.700	

De pH 3 à 12, on observe un seul saut bien dessiné et de hauteur constante. Les valeurs de $E_{\frac{1}{2}}$ observées sont très proches de celles données par PAGE *et al.*[8] pour l'acide *p*-nitrobenzoïque. Le pH a un effet très marqué sur les potentiels $E_{\frac{1}{2}}$ mais peu d'influence sur le courant de diffusion.

Étude théorique de la réduction polarographique. Partant de la relation:

$$E = E_{\frac{1}{2}} - \frac{0.059}{n} \log \frac{i}{i_d - i}$$

dans laquelle i est le courant de diffusion au potentiel E, i_d le courant de diffusion maximum et n le nombre d'électrons mis en jeu, nous tracerons la courbe

$$E = f\left(\log \frac{i}{i_d - i}\right)$$

TABLEAU III

Concentration phénylalanine	*pH*	*Point*	$i\ (\mu A)$	$E\ (V)$	i_d	$\log \frac{i}{i_d - i}$	n
$0.9 \cdot 10^{-3} M$	4	A	1.28	0.248	10.25	1.153—1	0.96
		B	2.88	0.272	10.25	1.590—1	0.85
		C	5.10	0.300	10.25	0	
		D	6.95	0.325	10.25	0.320	0.75
		E	9.30	0.360	10.25	0.990	0.99
$0.75 \cdot 10^{-3} M$	6	A	1.20	0.335	8.95	1.152—1	1.06
		B	2.88	0.365	8.95	1.670—1	1.12
		C	4.40	0.382	8.95	0	
		D	6.10	0.410	8.95	0.330	0.70
		E	7.65	0.440	8.95	0.770	0.78
$0.88 \cdot 10^{-3} M$	8	A	1.60	0.448	10.40	1.260—1	1.04
		B	3.36	0.472	10.40	1.680—1	1.06
		C	5.05	0.490	10.40	0	
		D	7.35	0.520	10.40	0.390	0.78
		E	9.75	0.554	10.40	1.180	0.90

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Les valeurs portées au Tableau III montrent que:

(1) étant donné l'allure des courbes, très proches des droites, il n'y a probablement qu'une réaction de réduction sur l'électrode à goutte.

(2) n est compris entre 0.7 et 1.12 V. Comme le nombre réel d'électrons est de 4 (voir p. 93), la réaction est irréversible.

Le potentiel $E_{\frac{1}{2}}$ variant avec le pH, la réaction de réduction sur l'électrode à goutte est de la forme:

$$\mathrm{Ox} + m\,\mathrm{H}^+ + n\,\mathrm{e} \rightleftarrows \mathrm{Red} + \frac{m}{2}\,\mathrm{H_2O}$$

Elle obéit à l'expression $E_{\frac{1}{2}} = E_0 - 0.059 \cdot \frac{m}{n}\,\mathrm{pH} + \frac{0.059}{n} \log \frac{K_{\mathrm{ox}}}{K_{\mathrm{red}}}$. Le dernier terme s'annule car $K_{\mathrm{ox}} \simeq K_{\mathrm{red}}$.

Dans le Tableau IV, nous donnons les valeurs des $E_{\frac{1}{2}}$ calculées d'après la formule ci-dessus pour des valeurs $\frac{m}{n}$ de 0.5, 1 et 2.

TABLEAU IV

LES VALEURS DES $E_{\frac{1}{2}}$ CALCULÉES

m/n \ pH:	1	2	3	4	5	6	7	8	9
0.5	0.13	0.16	0.19	0.22	0.25	0.28	0.31	0.34	0.37
1	0.16	0.22	0.28	0.34	0.40	0.46	0.52	0.58	0.64
2	0.22	0.34	0.46	0.58	0.70	0.82	0.94	1.06	1.18

Si on compare ces résultats à ceux donnés dans le Tableau II on peut admettre, bien que la réaction soit irréversible, que $\frac{m}{n} = 1$ pour la réaction de réduction polarographique de la phénylalanine nitrée.

Calcul de n par l'équation de Ilkovic. Seule la constante de diffusion D de notre composé n'est pas connue; nous lui attribuerons la valeur de $6.0 \cdot 10^{-6}$ cm²/sec donnée par PAGE, SMITH ET WALLER[8] pour l'acide *o*-nitrobenzoïque de structure semblable. En portant les valeurs obtenues lors de l'établissement de nos courbes d'étalonnage (p. 99) dans l'équation de Ilkovic, on obtient une valeur moyenne de $n = 4.1$ ($m = 1.92$ mg/ sec de mercure écoulé, $t = 4.6$ sec, hauteur de mercure 25 cm). Ces considérations nous permettent de conclure que le nitration de la phénylalanine avec $\mathrm{HNO_3}$ 10N donne un dérivé mononitré qui se réduit sur la goutte de mercure en hydroxylamine selon la réaction:

$$\mathrm{R{-}NO_2} + 4\,\mathrm{H}^+ + 4\,\mathrm{e} \rightarrow \mathrm{R{-}NHOH} + \mathrm{H_2O}.$$

Remarque. DENNIS ET POWELL[9] donnent comme constante de diffusion de l'acide *o*-nitrobenzoïque $D = 8.28 \cdot 10^{-6}$ cm²/sec. Dans ces conditions, n vaudrait 3.4.

Étude de quelques dérivés mononitrés voisins de la phénylalanine. Les 3 isomères de l'acide nitrobenzoïque ont été étudiés par PAGE *et al.*[8]. Nous avons examiné le comportement de ces composés de même que l'acide *p*-nitrophénylacétique de constitution très proche de la phénylalanine nitrée dans les conditions de notre méthode de dosage et qui n'a fait l'object d'aucune recherche polarographique à ce jour.

Des quantités croissantes de solutions alcooliques à 0.5% de ces différents acides sont introduites dans un ballon jaugé de 50 ml, on y a ajouté 5 ml de tampon pH 6 et 5 ml de KNO_3 *M*. On obtient ainsi des solutions en tout point semblables à celles de la phénylalanine nitrée avec, en plus, une faible quantité d'alcool (1 à 3%). Le Tableau V donne les valeurs de i_d à diverses concentrations.

TABLEAU V

COURBES D'ÉTALONNAGE DE DÉRIVÉS VOISINS

Concentration *M*	*i (μA)*			
	acide p-nitrophénylacétique	*acides nitrobenzoïques* *o-*	*m-*	*p-*
$0.3 \cdot 10^{-3}$			3.6	3.7
0.44	5.1			
0.5		6.2		5.9
0.6			7.2	7.5
0.8	9.3	9.7		
1.0	11.4	11.9	12.2	11.6
1.2	14.2	14.4	14.8	14.3

Les courbes d'étalonnage de l'acide *p*-nitrobenzoïque et *p*-nitrophénylacétique sont pratiquement superposables à celle de la nitrophénylalanine, celles des deux autres acides ont une pente un peu plus forte. Si, dans une solution de phénylalanine nitrée, on introduit de l'acide *p*-nitrobenzoïque, le polarogramme de ce mélange ne présent qu'une vague parfaitement dessinée comme s'il n'y avait qu'un seul composé et l'augmentation de la hauteur du saut est proportionnelle à la quantité ajoutée. Ainsi il est possible d'utiliser cet acide comme étalon interne (voir p. 98). L'étude de ces trois composés en fonction du pH conduit aux mêmes conclusions que celles données à propos de la phénylalanine nitrée.

TABLEAU VI

pH	$E_{1/2}$ *(V)*		
	acides nitrobenzoïques *p-*	*m-*	*acide p-nitrophénylacétique*
2.3	0.17	0.18	0.18
4.0	0.28	0.29	0.30
5.8	0.39	0.41	0.42
8.0	0.53 0.83	0.64	0.59
10.5	0.70	0.70	0.72

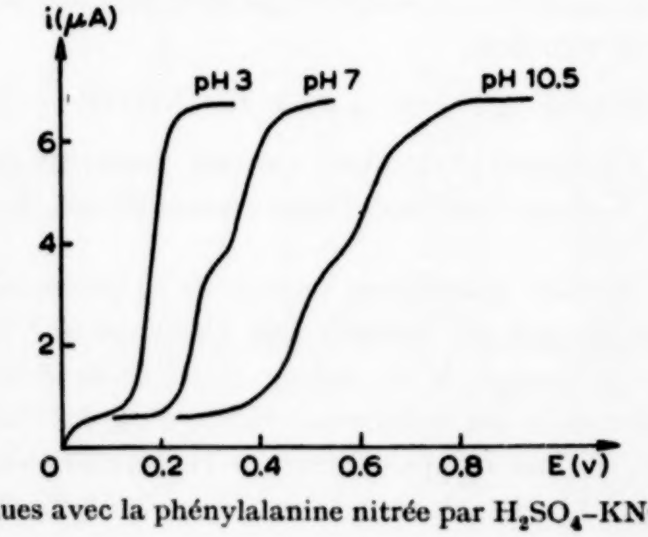

Fig. 2. Courbes obtenues avec la phénylalanine nitrée par H_2SO_4–KNO_3. $C = 0.25 \cdot 10^{-3} M$.

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Étude des courbes polarographiques de la phénylalanine nitrée par un mélange H_2SO_4 conc. - KNO_3

33 mg de phénylalanine sont nitrés par le mélange de 1 ml H_2SO_4 conc. et 0.2 g KNO_3 au bain-marie pendant 1 h. Après neutralisation par KOH, le volume est porté à 100 ml. Des parties aliquotes de 10 ml sont additionnées de 20 ml de solution tampon, de 3 gouttes de rouge de méthyle et portées à 100 ml (voir Tableau X, p. 99).

Dès le pH 4.5, les polarogrammes présentent 2 ou 3 vagues souvent mal séparées (voir Fig. 2). Au pH 6, on obtient des courbes bien dessinées et reproductibles, c'est celui-ci que nous retiendrons pour le dosage de la phénylalanine (voir p. 98); on mesurera le saut total.

Le Tableau VII donne le courant de diffusion de quelques composés voisins de la nitrophénylalanine polarographiés dans les mêmes conditions que cette dernière avec en plus 1% d'alcool.

TABLEAU VII

Concentration M	*i (µA)*		
	acides dinitrobenzoïques 2, 4	*3, 5*	*ac. trinitrobenzoïque 2, 4, 6*
$0.195 \cdot 10^{-3}$			7.8
0.235	6.0	5.3	
0.39			14.7
0.47	11.5	11.8	
0.78			30.2
0.94	22.3	21.8	
1.17			43.5
1.41	32.9	33.4	

Les courbes d'étalonnage des acides 2,4- et 3,5-dinitrobenzoïques sont superposables et de pente légèrement plus faible que celle de la phénylalanine nitrée. À concentration molaire égale, le courant de diffusion des acides dinitrobenzoïques est le double de celui des acides mononitrés. En appliquant la formule de Ilkovic, on trouve $n = 8$ pour les acides 2,4- et 3,5-nitrobenzoïques de même que pour la phénylalanine nitrée avec H_2SO_4 conc. - KNO_3 et $n = 12$ pour l'acide trinitrobenzoïque, ce qui prouve que les fonctions nitro de tous ces composés sont réduites en hydroxylamine.

On observe en outre que les acides dinitrobenzoïques donnent une vague polarographique en milieu acide et deux en milieu alcalin alors que la phénylalanine, nitrée par H_2SO_4 conc. - KNO_3, donne un saut en milieu acide et trois en milieu alcalin avec en plus deux légers points d'inflexion. Quant à la hauteur des sauts de cette dernière, ils correspondent sensiblement à ceux des acides „dinitro". Pourtant la complexité des courbes prouvent que nous sommes en présence d'un mélange avec prédominance de composés dinitrés. Ces observations seront confirmées par l'étude chromatographique dont nous donnons les résultats à la page 97.

Remarques sur la réduction polarographique des dérivés nitrés

Pearson[10] a étudié systématiquement le comportement polarographique des nitrobenzènes, nitrotoluènes, nitrophénols et nitrorésorcinols. Cette réduction met en jeu 4 électrons lorsque le milieu est neutre ou alcalin (stade hydroxylamine) et 6 électrons en milieu acide (pH 2.5). Le *m*-dinitrobenzène produit deux sauts et met en jeu 8 électrons en milieu neutre ou alcalin et présente 3 sauts correspondant à 12 électrons en milieu acide. Les polarogrammes des deux autres isomères se caractérisent par des stades intermédiaires en milieu neutre, un groupe se réduit en amine, l'autre en hydroxylamine avec un échange total de 10 électrons. Le second groupe augmente le potentiel de réduction du premier. Cet effet est particulièrement marqué pour les dérivés *o* et *p*.

Le *m*-nitrophénol se réduit jusqu'au stade hydroxylamine (4 e) sauf en milieu très acide pour lequel on a formation d'amine (6 e). Les deux autres isomères se réduisent en amine. Les dinitrophénols mettent en jeu, à presque tous les pH, 10 électrons. Un des groupes nitro se transforme en hydroxylamine, l'autre en amine. PAGE, SMITH ET WALLER[8] ont examiné toute une série de dérivés nitrés, entre autres les 3 acides mononitrobenzoïques. Leurs conditions de travail sont quelque peu différentes des nôtres. En milieu tamponné et en présence de 10% d'alcool, ils obtiennent une vague en milieu neutre et deux en milieu acide et alcalin avec mise en jeu de 4 e en dessus du pH 4 et de 6 e en dessous. DENNIS, POWELL ET ASTLE[9] ont effectué la polarographie des acides nitrobenzoïques en milieu tamponné mais sans adjonction d'alcool. Ils obtiennent des sauts avec une seule vague sauf pour le dérivé *meta* qui donne deux vagues en milieu alcalin. Dans tous les cas, il y a échange de 4 électrons. On peut donc affirmer que la réduction des groupes nitro dépend non seulement du pH mais aussi des ions étrangers et surtout de la présence d'alcool. Nous avions du reste déjà fait une remarque analogue à propos d'une étude précédente[11].

Nous avons reproduit dans les Figs. 1 et 2 les polarogrammes de la phénylalanine nitrée à divers pH. Les polarogrammes des acides mononitrobenzoïques et nitrophénylacétique sont analogues à ceux de la phénylalanine nitrée par HNO_3 10*N*. Les acides dinitrobenzoïques donnent un saut en milieu acide et neutre et trois en milieu alcalin. Nous n'avons jamais observé de réduction allant jusqu'au stade amine.

Étude chromatographique des solutions de phénylalanine nitrée

Afin de connaître la constitution des solutions de phénylalanine nitrée, nous en avons effectué une étude chromatographique. La phénylalanine est susceptible de donner des dérivées mono-, di- et trinitrés; il peut en outre se former des produits de dégradation par oxydation de la chaîne latérale, soit avant, soit après la nitration sur le noyau. Nous avons appliqué la technique de chromatographie ascendante sur papier Schleicher et Schull No. 2043 b en partant de volumes compris entre 0.005 et 0.01 ml. Pour des essais au papier tamponné, celui-ci a été préalablement immergé dans un mélange à parties égales de phosphates mono- et disodiques 0.1*M*, puis égoutté et séché à la température du laboratoire.

Les dérivés nitrés à l'état pur et cristallisés sont dissous dans l'alcool à une concentration de 1 g/l. Pour la préparation des mélanges de nitration avec HNO_3 ou H_2SO_4 conc.-KNO_3, voir p. 90. Le mélange est porté directement sur le papier sans neutraliser. D'autre part, nous avons renoncé à une désalification, car dans nos conditions de travail, les ions inorganiques ne gênent pas.

Après un grand nombre d'essais nous proposons d'utiliser les mélanges suivants:

I. Isopropanol 30, acétone 15, eau 6, acide acétique glacial 6.
II a. Même système dans la proportion 30, 15, 18, 9.
II b. Même système que ci-dessus, mais avec papier tamponné.
III a. Éthanol 80, ammoniaque conc. 5, eau 15.
III b. Même système, avec papier tamponné.

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Les divers dérivés nitrés étant faiblement colorés, nous révélons leur présence de la façon suivante: après séchage de la feuille, on pulvérise une solution de chlorure stanneux à 1% dans l'acide chlorhydrique 0.5*N*. On sèche sous infra-rouge puis on pulvérise une solution de *p*-diméthylaminobenzaldéhyde (DAB) à 1% dans un mélange alcool-HCl 0.5*N* (1:1). Les dérivés nitrés donnent des spots jaunes à orangés. Ce réactif permet de déceler jusqu'a 0.05γ de di- et trinitro et 0.1 γ de mononitro.

Nous avons aussi utilisé la ninhydrine en solution à 0.3% dans le butanol pour révéler la phénylalanine. Après chauffage à l'étuve à 90° durant 5 min, les spots de la phénylalanine se colorent en violet. La phénylalanine nitrée produit la même coloration, elle peut donc être révélée par son groupe nitro et par ses fonctions amino-acides. Ces deux processus peuvent être successivement mis en oeuvre sur le même chromatogramme. On révèle tout d'abord les acides aminés par la ninhydrine, note l'emplacement des taches, puis on pulvérise la solution de chlorure stanneux, les spots violets disparaissent et ceux des composés nitro et dinitro se forment après pulvérisation de la *p*-diméthylaminobenzaldéhyde.

Résultats

Les chromatogrammes ont été effectués sur 30γ de substance. Les derniers résultats du Tableau VIII proviennent de solutions de nitration, oxydées par quelques cristaux de permanganate puis décolorées par l'eau oxygénée.

TABLEAU VIII

	R_F				
	I	*II*		*III*	
		a	*b*	*a*	*b*
Acide *o*-nitrobenzoïque	0.88	0.96	0.69	0.73	0.78
Acide *m*-nitrobenzoïque	0.96	0.97	0.97	0.77	0.79
Acide *p*-nitrobenzoïque	0.97	0.97	0.97	0.75	0.78
Acide *p*-nitrophénylacétique	0.98	0.99	L	0.73	0.75
Acide 2,4-dinitrobenzoïque	0.99	0.99	1	0.69	0.69
Acide 3,5-dinitrobenzoïque	0.84	0.94	0.96	0.75	0.76
Acide 2,4,6-trinitrobenzoïque	0.99	0.99	1	0.85	0.85
Phénylalanine	0.33	0.68	0.68	0.64	0.71
Phénylalanine nitrée pár HNO_3 10*N*	0.34	0.80	0.75	0.54	0.42
	0.90	0.97	0.96	0.72	0.71
	0.98	0.99	1	0.85	0.83
Phénylalanine nitrée par H_2SO_4-KNO_3	0.38	0.72	0.72	0.55	0.59
	0.73	0.83	0.95	0.69	0.69
	0.85	0.95	1	0.75	0.77
	0.99	0.99		0.85	0.83
Phénylalanine nitrée par HNO_3 10*N* et oxydée				0.73	
				0.75	
Phénylalanine nitrée par H_2SO_4-KNO_3 et oxydée				0.69	
				0.75	

Interprétation des résultats

Il n'est pas aisé de différencier les acides nitrobenzoïques. Il faut pour cela tenir compte des résultats obtenus à l'aide des mélanges de solvants I, IIb, IIIa. Les

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résultats fournis par les acides benzoïques manquent de netteté, les R_F sont très voisins quels que soient les éluants employés. La nitrophénylalanine est par contre facilement identifiable, le R_F étant beaucoup plus faible que ceux des autres dérivés nitrés. Ce fait tient probablement à la présence de la chaîne latérale. La phénylalanine nitrée par HNO_3 10*N* donne une tache principale, révélée en violet par la ninhydrine et en jaune par la DAB. Nous avons probablement de la mononitrophénylalanine.

Sur le même chromatogramme, nous percevons un second spot double faible qui correspond à ceux des acides *o*- et *p*-nitrobenzoïques à une concentration de 2% env. On ne trouve pas de phénylalanine, ce qui permet donc de conclure que ce mélange de nitration renferme approximativement 98% de nitrophénylalanine et 2% d'acide nitrobenzoïque. On décèle en outre des traces négligeables d'acide trinitrobenzoïque. Dans ce même mélange après oxydation par le permanganate, on ne trouve plus de nitrophénylalanine; elle a été quantitativement oxydée en un mélange d'acides *o*- et *p*-nitrobenzoïques.

La nitration au moyen de H_2SO_4-KNO_3 fournit un mélange plus complexe. Le spot principal révélé par le DAB correspond à la 2,4-dinitrophénylalanine tandis que les deux autres spots proviennent sans doute des acides 2,4 et 3,5-dinitrobenzoïques. On décèle aussi des traces d'acide trinitrobenzoïque. On constate enfin l'absence totale de phénylalanine. L'analyse semiquantitative montre que ce mélange est constitué de 60% de dinitrophénylalanine, 30% d'acide 2,4-nitrobenzoïque et 10% d'acide 3,5-dinitrobenzoïque. Après oxydation au permanganate ce mélange ne renferme plus de dinitrophénylalanine, il y a 90% d'acide 2,4-dinitrobenzoïque et 10% d'acide 3,5- dinitrobenzoïque.

II. MÉTHODE DE DOSAGE DE LA PHÉNYLALANINE

Les considérations qui précèdent montrent que le dosage par nitration est possible aussi bien avec HNO_3 10*N* qu'avec le mélange H_2SO_4-KNO_3. En effet, dans le premier cas, il se forme presqu'uniquement de la nitrophénylalanine (98%). La position et la hauteur des sauts dues à l'acide nitrobenzoïque étant égales à celles de la nitrophénylalanine, ceux-ci ne gênent donc pas. Même remarque pour le second cas.

Mode opératoire

La substance pesée est introduite dans un tube à fond plat de 10 cm de long et de 2 cm de diamètre. (Si l'échantillon est une solution, on évapore à l'étuve à 90°). On ajoute 0.5 ml de HNO_3 10*N* et on porte à l'ébullition pendant $1\frac{1}{2}$ h par chauffage sur plaque électrique. Le reflux est assuré par une éprouvette de diamètre légèrement inférieur au tube et dans laquelle on fait circuler de l'eau froide. Après nitration, on laisse refroidir, on neutralise avec une solution de KOH *N* en présence de rouge de méthyle. On introduit la solution dans un ballon jaugé de 10 ml, on ajoute 5 ml au tampon pH 6. On chasse l'oxygène par un courant d'hydrogène pendant 10 min et on polarographie. Les résultats sont donnés dans le Tableau IX.

Le dosage est réalisable pour des concentrations comprises entre $2.4 \cdot 10^{-4}$ et $6 \cdot 10^{-3} M$ avec une erreur inférieure à 2.5%. Pour des concentrations plus élevées, les valeurs obtenues sont trop faibles. La quantité minimum dosable est de l'ordre de 30 γ dans 10 ml soit $2 \cdot 10^{-5} M$. L'erreur atteint alors 12%.

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TABLEAU IX

COURBE D'ÉTALONNAGE

Prise (mg)	*Concentration effective (M)*	*i (μA)*	$E_{1/2}$	*Concentration trouvée (M)*	*Erreur*
0.05	$3.03 \cdot 10^{-5}$	0.48	0.60	$3.25 \cdot 10^{-5}$	+ 6%
0.10	6.06	0.96	0.58	6.78	+12
0.20	$1.21 \cdot 10^{-4}$	1.55	0.60	$1.25 \cdot 10^{-4}$	+ 3.3
0.30	1.82	2.28	0.58	1.88	+ 3.4
0.40	2.42	2.96	0.58	2.47	+ 2
0.50	3.03	3.68	0.59	3.08	+ 1.6
0.78	5.20	6.30	0.58	5.30	+ 2
1.00	6.06	7.12	0.58	6.21	+ 2.4
1.29	7.80	9.35	0.59	7.97	+ 2.2
1.65	$1.00 \cdot 10^{-3}$	11.85	0.60	$1.04 \cdot 10^{-3}$	+ 0.4
1.65	1.00	11.45	0.59	0.97	— 3
2.11	1.28	14.70	0.58	1.25	— 2.5
3.00	1.82	20.80	0.60	1.80	— 1
5.00	3.03	36.80	0.59	3.06	+ 1
10.00	6.06	72.00	0.59	6.03	— 0.5

Pour éviter les erreurs dues à l'appareillage, on peut procéder par étalon interne en prenant comme standard l'acide *p*-nitrobenzoïque qui se comporte comme la phénylalanine nitrée (voir p. 94).

Remarque. On peut aussi doser la phénylalanine par nitration au mélange H_2SO_4-KNO_3. On procède comme il a été dit précédemment et le polarogramme se fait au pH 6 (voir Tableau X).

TABLEAU X

COURBE D'ÉTALONNAGE POUR LA NITRATION PAR H_2SO_4-KNO_3

Prise mg	*Concentration réelle*		*i (μA)*	*Conc. trouvée M*	*Erreur*
	g/l	*M*			
0.50	0.010	$0.61 \cdot 10^{-4}$	1.60	$0.60 \cdot 10^{-4}$	— 1.7%
1.00	0.020	1.21	3.30	1.25	+ 3
1.70	0.034	2.06	4.75	1.90	— 8
2.75	0.055	3.34	8.50	3.40	+ 1.8
3.00	0.060	3.63	8.80	3.55	— 2.1
5.00	0.100	6.06	15.00	6.10	+ 0.8
5.50	0.110	6.70	16.60	6.70	0
10.00	0.200	$1.21 \cdot 10^{-3}$	29.80	1.22	+ 0.8

Sélectivité

Dans les conditions des deux méthodes de dosages décrites, l'histidine ne gêne pas; par contre, la tyrosine et le tryptophane produisent des sauts que se superposent à celui de la phénylalanine. Il est possible d'éliminer complètement la tyrosine par oxydation du mélange à 60° après nitration au moyen de quelques cristaux de permanganate dont l'excès est détruit par un peu d'eau oxygénée. Le manganèse ainsi introduit ne gêne pas. La phénylalanine est aussi oxydée mais le saut ne subit pas de modification car la réaction a lieu sur la chaîne latérale et donne de l'acide *p*-nitrobenzoïque. Quant au saut du tryptophane, il est réduit de 70% environ. Il ne nous a pas été possible de l'éliminer complètement par ce moyen. Une étude plus complète à ce sujet sera publiée prochainement.

RÉSUMÉ

Ce travail comprend l'étude des conditions de nitration de la phénylalanine puis une recherche de la nature des constituants résultant de cette opération, à l'aide de la polarographie et de la chromatographie. Parallèlement, quelques acides nitrobenzoïques qu'on trouve dans les produits de nitration de la nitrophénylalanine, ont été examinés par ces deux processus.

Une méthode de dosage polarographique de la phénylalanine a été proposée qui permet de déceler jusqu'à 30 γ de phénylalanine dans 10 ml de solution. Entre $2.4 \cdot 10^{-4} M$ et $6 \cdot 10^{-3} M$, l'erreur reste inférieure à 2.5%. Elle atteint 12% pour des concentrations de l'ordre de $2 \cdot 10^{-5} M$.

SUMMARY

This paper comprises a study of the conditions for nitrating phenylalanine and an investigation of the compounds obtained, polarographic and chromatographic methods being employed. At the same time some nitrobenzoic acids that are found among the nitration products of nitrophenylalanine were examined by both these methods.

A method has been proposed for the polarographic determination of phenylalanine, by means of which as little as 30 γ of this substance can be detected in 10 ml solution. With concentrations between $2.4 \cdot 10^{-4} M$ and $6 \cdot 10^{-3} M$, the error is less than 2.5%, with those of the order of $2 \cdot 10^{-5} M$ it approaches 12%.

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Reçu le 30 octobre 1957

ACTIVATION ANALYSIS OF VANADIUM IN HIGH ALLOY STEELS USING MANGANESE AS INTERNAL STANDARD

by

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INTRODUCTION

The determination of small amounts of vanadium in high alloy steels has always presented a rather difficult problem. Usually this element is determined by potentiometric, amperometric or coulometric titration or by spectrophotometry. In all of these methods, special precautions or separations are necessary to avoid interference from other constituents. Moreover, the presence of tungsten causes unavoidable losses, due to the adsorption of vanadium on tungstic acid. As vanadium has a rather large cross-section for thermal neutrons, the determination of this element by radioactivation was investigated.

Radioactivation of traces of vanadium in crude oil has been studied by BROOKSBANK, LEDDICOTTE AND MAHLMAN[1], while BROOKSBANK, LEDDICOTTE AND REYNOLDS[2] determined this element in titanium and its alloys.

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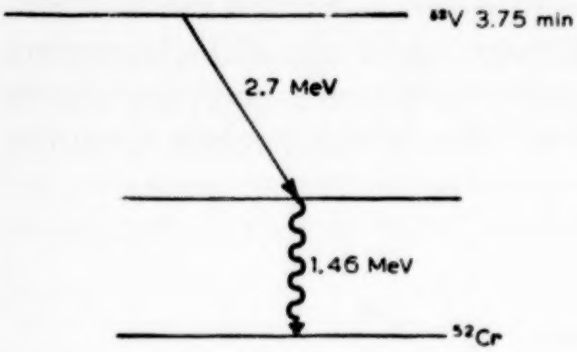
NUCLEAR DATA



Natural vanadium, consisting of the single isotope ^{51}V, gives rise to only one product by (n,γ) reaction, namely ^{52}V, a beta-gamma emitter, having a half-life of 3.75 min. The activation cross-section is 4.5 barns.

INTERFERING ACTIVITIES

Since the half-life of ^{52}V is too short to permit isolation of this element after irradiation, interfering activities due to (n,γ) reactions on a number of constituents is to be expected. The radiochemical properties of the most usual constituents in high alloy steels are summarized in Table I.

TABLE I

RADIOCHEMICAL PROPERTIES OF STEEL CONSTITUENTS, SUBJECT TO ACTIVATION BY THERMAL NEUTRONS

Target nuclide	*% Abundance*	*Activation cross-section σ (barns)*	*(n,γ) reaction product*	$T_{\frac{1}{2}}$	*Radiation and energy*
^{30}Si	3.05	0.11	^{31}Si	2.62h	β^-1.47
^{31}P	100	0.23	^{32}P	14.3 d	β^-1.70
^{34}S	4.2	0.26	^{35}S	87 d	β^-0.16
^{36}S	0.016	0.14	^{37}S	5.0 m	β^-1.6/4.3; γ 2.7
^{50}Ti	5.34	0.14	^{51}Ti	5.8 m	β^-1.9/2.2; γ 0.32
^{51}V	∼100	4.5	^{52}V	3.75m	β^-2.7; γ 1.46
^{54}Cr	2.38	0.3	^{55}Cr	3.52m	β^-2.8
^{55}Mn	100	13.4	^{56}Mn	2.58h	β^-2.81/1.04/0.73; γ 0.82/1.81/2.13
^{54}Fe	5.84	0.7	^{55}Fe	3.0 y	E.C. ε 0.21
^{58}Fe	0.31	0.7	^{59}Fe	45.1 d	β^-0.46/0.27; γ 1.10/1.29
^{59}Co	100	100	^{60m}Co	10.5 m	γ 0.058
		6	^{60}Co	5.2 y	β^-0.306; γ 1.17/1.33
^{58}Ni	67.7	4.2	^{59}Ni	10^5 y	E.C. ε 1.07
^{62}Ni	3.66	15	^{63}Ni	85 y	β^-0.065
^{64}Ni	1.16	2.6	^{65}Ni	2.56h	β^-2.10/1.10/0.60 γ 1.49/1.12/0.37
^{63}Cu	69.1	4.3	^{64}Cu	12.8 h	E.C., β^-0.571; β^+0.66 γ 1.34
^{65}Cu	30.9	2.1	^{66}Cu	5.1 m	β^-2.63/1.59; γ 1.04
^{93}Nb	100	1.0	^{94m}Nb	6.6 m	I.T. : 0.042
^{98}Mo	23.75	0.13	^{99}Mo	67 h	β^-1.23/0.45; γ 0.04 to 0.78
^{100}Mo	9.62	0.20	^{101}Mo	14.6 m	β^-1.2/2.2; γ 0.191/0.96
^{181}Ta	100	21	^{182}Ta	113 d	β^-0.51; γ 0.334 to 1.18
^{184}W	30.6	2.1	^{185}W	73 d	β^-0.43/0.37; γ 0.058
^{186}W	28.4	34	^{187}W	23.9 h	β^-0.62/1.33; γ 0.072 to 0.78

It appears from Table I that, when a short irradiation time is used, the activity of a large number of isotopes will be negligible, the cross-sections being small or the half-lives large in comparison with those of ^{52}V. Furthermore, interferences can be reduced by making use of a gamma-spectrometer, restricting the measurements to gamma energies within a band ranging from 1.3 to 1.55 MeV. It appears that under these experimental conditions, the only radiations giving appreciable interference are the 1.81 and 2.13 MeV gammas of ^{56}Mn, which produce Compton recoil pulses in the energy band in question.

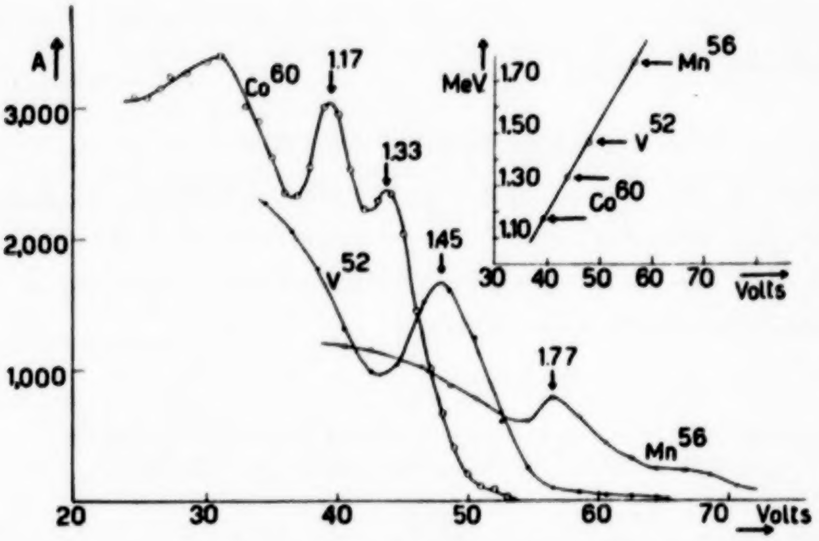


Fig. 1. Gamma spectrum of V, Co and Mn.

Fig. 1 represents the gamma spectra of ^{52}V and ^{56}Mn measured with a band width from 1.3 to 1.55 MeV. A spectrum of ^{60}Co is also included, to provide the necessary calibration peaks. It is obvious that a correction for the interference due to ^{56}Mn can easily be made by analysing the decay curve of the irradiated sample, since the half-life is very different from that of ^{52}V.

Interference due to the presence of ^{65}Ni, half-life 2.56 h, may be regarded as negligible, since ^{64}Ni occurs only to the extent of 1.16% in the natural element. Furthermore, the activation cross-section is rather small ($\sigma = 2.6$ barns), and the 1.49 MeV gamma amounts to only 25% in the decay scheme of ^{65}Ni.

Possible interferences from ^{52}Cr and ^{55}Mn, which give rise to ^{52}V by (n,p) and (n,α) reactions with fast neutrons, were investigated, using the Belgian Reactor BR1. Samples of Cr as $(NH_4)_2Cr_2O_7$ and Mn as $MnAc_2 \cdot 4H_2O$ were irradiated in plastic capsules for periods of 10 sec. At the site of irradiation near the reflector, the neutron flux was approximately 10^{10}n/cm^2/sec, whereas the cadmium ratio at the same place was about 280. The activity of the samples was measured in 4-ml standard vials, using a Tracerlab RLD-3 well-type spectrometer detector connected to an MBLE gamma spectrometer. Bias voltage and window were set to measure gamma radiation between 1.3 and 1.55 MeV. Results for 51.7 mg of Mn, 149 mg of Cr and 13.9 mg of V are illustrated in Fig. 2.

It appears that under these experimental conditions, the specific activity of ^{52}V at t_0 amounts to 5,600 counts sec/mg vanadium, the half-life corresponding to 3.75 min. The analysis of the decay curve of Mn indicates that no appreciable amount of ^{52}V is formed by an (n,α) reaction, whereas the specific activity of ^{56}Mn amounts to 22.3 counts/sec/mg.

The analysis of the decay curve of the chromium sample shows that ^{52}V is formed to an extent of 0.047 counts/sec/mg Cr. Consequently, even a Cr/V ratio of 1000/1 will produce an error of less than 1%, by the (n,p) reaction on chromium. The analysis of the decay curve of chromium shows that a longer-lived isotope is present with a specific activity of 0.14 counts/sec/mg Cr. This half-life of about 1.5 h does not correspond to any known chromium isotope and was assumed to be caused by an impurity in the chromium sample.

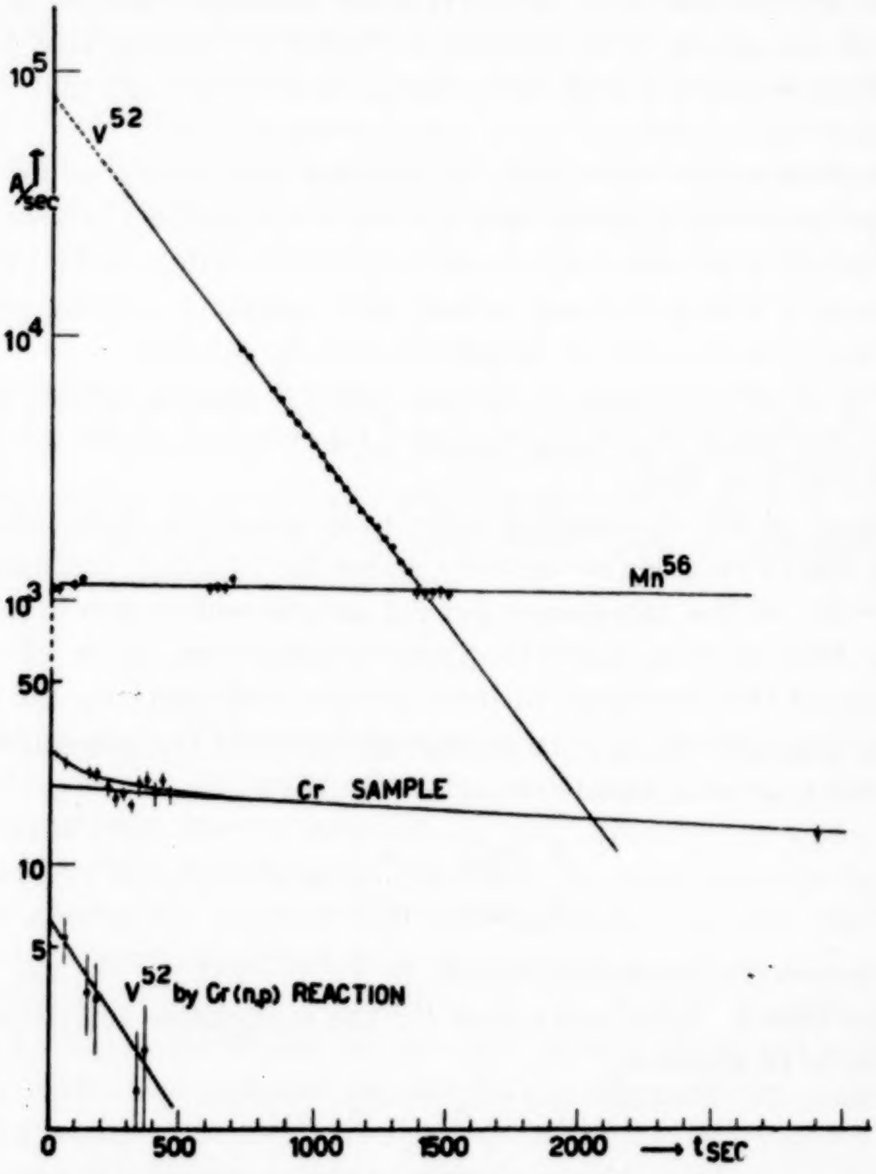


Fig. 2. Interference by (n,p) and (n,α) reactions.

It should be stressed that activation with neutrons having a less favorable cadmium ratio, can produce a significant amount of ^{52}V. Activations were carried out, for example, with the Amsterdam cyclotron, using 26 MeV deuterons on a Be target as a neutron source. The neutron flux was approximately 10^7 n/cm^2/sec in the paraffin block used as a moderator. The paraffin block, 20 cm in diameter, was rotated close to the target outside the cyclotron. The cadmium ratio, determined by means of a gold foil, as described by MARTIN[3], was approximately 7.

It appeared that a Cr/V ratio of 1000/1 would cause the determination of vanadium to be too high by 220%. No ^{52}V could be detected in a manganese sample, irradiated under identical conditions.

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CORRECTION OF NEUTRON FLUX VARIATIONS USING AN INTERNAL STANDARD

The accuracy of an analysis by radioactivation will mainly depend on the homogeneity of the neutron flux in the sample and the reference, all other factors being equal. In some cases, important errors may also arise from different neutron shadowing in sample and reference. Furthermore, the short half-life of the isotope under investigation does not allow control by more than one reference sample. These restrictions can be greatly reduced by the use of an internal standard. The discussion of the proposed internal standard radioactivation procedure will be restricted to the determination of vanadium. The method is, however, appropriate to other cases, the only condition required being the presence of a second element that also gives rise to a radioactivity measurable with good accuracy.

For the determination of vanadium, manganese was chosen as an internal standard. For this purpose two approximately equal steel samples, *a* and *b* mg respectively, are irradiated simultaneously in a suitable neutron flux. Before the irradiation, *c* mg of vanadium is homogeneously mixed with sample 2, *c* being preferably large in comparison with the amount of vanadium already present.

A decay curve of both samples is plotted, using a gamma spectrometer, the bias voltage and the window width being regulated for counting within a band of energies ranging from 1.3 to 1.55 MeV.

After the decay of ^{52}V, the residual activity is caused by ^{56}Mn, which is the only element giving rise to appreciable activity under the existing conditions. Any difference in the activity of the manganese per mg sample will be due to inhomogeneities of the neutron flux or to a different neutron shadowing. It is obvious that the specific activities of the vanadium in both samples will differ by the same fraction.

Assuming $A_{t,\,(\mathrm{Mn})}$ and $A'_{t,\,(\mathrm{Mn})}$ to be the activities of the manganese in samples 1 and 2 at a time t, after complete decay of ^{52}V, then:

$$\frac{A_{t,\,(\mathrm{Mn})}}{A'_{t,\,(\mathrm{Mn})}} = \frac{a}{b} \times \alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where α is the activation correction factor. If $A_{t_0,\,(\mathrm{V})}$ and $A'_{t_0,\,(\mathrm{V})}$ are the vanadium activities at the time t_0, after correction for the manganese activities, the following relations can easily be deduced:

$$A_{t_0,\,(\mathrm{V})} = A_{t_0} - A_{t_0,\,(\mathrm{Mn})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

$$A'_{t_0,\,(\mathrm{V})} = A'_{t_0} - A'_{t_0,\,(\mathrm{Mn})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where A_{t_0} and A'_{t_0} are the total activities, while $A_{t_0,\,(\mathrm{Mn})}$ and $A'_{t_0,\,(\mathrm{Mn})}$ are the manganese activities at a time t_0.
Further,

$$S_{t_0,\,(\mathrm{V})} = \frac{1}{c}\left[A'_{t_0,\,(\mathrm{V})} \times \alpha - \frac{b}{a} \times A_{t_0,\,(\mathrm{V})}\right] \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where $S_{t_0,\,(\mathrm{V})}$ is the specific activity of ^{52}V at t_0 in counts per mg and per second. The vanadium content will then be given by:

$$\%\,\mathrm{V} = \frac{A_{t_0,\,(\mathrm{V})} \times 100}{a \times S_{t_0,\,(\mathrm{V})}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

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ACCURACY

As can be deduced from equation (4), the accuracy of the internal standard method is determined by:

1. Accuracy of the activation correction factor α, which, in turn, will mainly depend upon the accuracy with which the manganese activities can be measured. This accuracy involves such factors as manganese content of the sample, manganese to vanadium ratio, irradiation time, neutron flux, sample size, etc.
2. Amount of vanadium added to sample 2, which determines the accuracy of the specific activity S_{t_0}, (V). As c is made larger, the error in S_{t_0}, (V) decreases. The amount should preferably be large, compared to the amount of vanadium already present in sample 2.
3. The size a and b of the samples, which will depend on the vanadium content and neutron fluxes available; they should be of the same order so as to keep the value of α close to unity.

RESULTS

The accuracy of the method was tested on a number of National Bureau of Standard steel samples with widely varying composition. The Belgian reactor BR1 was used as a neutron source for samples having a large Cr/V ratio, so as to avoid interference of the (n,p) reaction on ^{52}Cr. In some other cases, the Amsterdam cyclotron was used (26 MeV deuterons on a Be target).

Procedure

Two weighed samples of the steel turnings to be analysed are placed in plastic capsules, the sample size depending on the vanadium content and neutron flux available. An accurately known amount of pure ammonium vanadate is added to one of the samples and homogeneously mixed. The samples are activated for 10 to 60 sec, depending upon the neutron flux and vanadium content. After irradiation, the plastic capsules are transferred to a standard vial fitting a Tracerlab RLD3 well-type spectrometer detector connected to an MBLE gamma spectrometer. Voltage bias and window width are set to count gamma radiation between energies of 1.3 and 1.55 MeV. The samples are alternately counted for periods of 20 sec, with a lapse of 10 sec between successive periods. After the decay of ^{52}V, the manganese activity is measured using 200 sec counting periods with 10 sec lapses between periods as before. The decay curves are plotted on semi-log paper and analysed for the manganese and vanadium activities. A typical plot is represented in Fig. 3 for NBS steel sample 101d, irradiated during 10 sec in BR1, at 10^{10} n/cm^2/sec.

The value of α is determined from the ratio of the manganese activities. The vanadium activities are extrapolated to t_0 and the vanadium content calculated from the values A_{t_0}, (V) and A'_{t_0}, (V) according to equations (4) and (5).

Results of analyses as given in Table II were in excellent agreement with the results of the N.B.S. In fact, for small amounts of vanadium, the precision is as good as that obtained in chemical analysis. The standard error on 8 analyses made in different laboratories on sample 155, for instance, was 27%, as is apparent from the NBS certificate, whereas the standard error on 7 analyses by radioactivation was

TABLE II

ACTIVATION ANALYSIS RESULTS

NBS standard sample	*%V*	*%Mn*	*%Cr*	*%W*	*%Ni*	*Sample weight (mg)*			α	*counts/sec* $At_{o'}(V)$	*counts/sec* $A't_{o'}(V)$	*%V found by activation analysis*
						a	*b*	*c*				
155*						296.7	447.2	3.236	1.062	24.5	1,516	0.0170
						604.5	610.4	5.942	1.046	28.4	2,510	0.011
Cr–W steel	0.014	1.24	0.485	0.517	0.100	600.3	824.4	9.806	0.979	3.5	384.0	0.017_4
						642.9	654.9	8.605	1.062	29	2,130	0.017_4 $\sigma\% = 15.8$
						657.5	548.8	15.077	1.079	3.65	578	0.013_4
						527.3	649.3	13.684	1.044	4.7	840	0.014
						661.4	793.6	8.470	1.028	26.4	1,920	0.017_4
												$\overline{m} = 0.015_3 \pm 0.0024$
161*						336.8	132.3	2.190	0.9023	55	1,620	0.025
						397.4	363.9	5.358	1.108	87	3,800	0.028_5 $\sigma\% = 10._2$
Ni–Cr casting alloy	0.029	1.28	16.88	—	64.29	332.7	504.3	3.620	1.063	19.2	680	0.030
						472.7	412.3	7.490	0.961	64.8	3,400	0.032
												$\overline{m} = 0.029 \pm 0.0029$
101d*						36,198	403.6	6.998	1.236	82	2,868	0.046
						193.3	205.9	1.521	1.074	76	1,316	0.045 $\sigma\% = 7._9$
Cr–Ni steel	0.049	0.739	18.68	—	9.05	223.8	239.7	5.273	1.007	62.5	3,122	0.048
						221.5	386.9	3.877	1.059	47.5	1,530	0.054
												$\overline{m} = 0.048_3 \pm 0.038$
153**						1,137.3	937.2	26.28	0.995	66.2	133.60	1.95
						640.6	474.3	21.74	0.882	44.0	115.20	2.16
Co–Mo–W steel	2.04	0.219	4.14	1.58	0.107	640.8	634.2	11.95	0.985	63.2	129.60	1.81
												$\overline{m} = 1.97 \pm 0.17$

* 10 seconds irradiation in BR1 reactor neutron flux from 10^9 up to 10^{10} n/cm^2/sec, Cd ratio 280.

** 60 seconds irradiation with Amsterdam cyclotron, neutron flux 10^7 n/sec, Cd ratio 7.

15.8%. For sample 101d the average value given is 0.049%, the standard error on 10 analyses being 5.6%, whereas the corresponding error on 4 radioactivations is 7.9%.

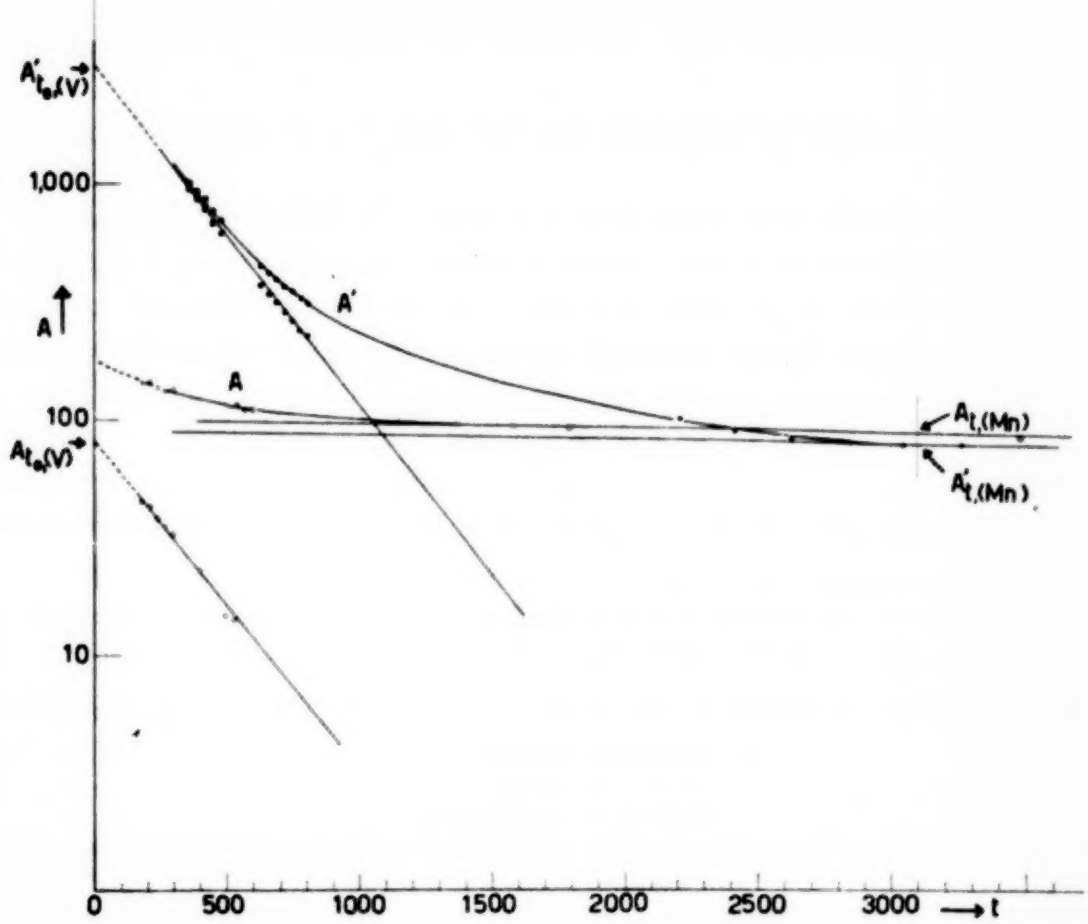

Fig. 3. Determination of vanadium with internal standard.

ACKNOWLEDGEMENTS

Acknowledgements are due to Prof. Dr. A. H. ATEN Jr. for the hospitality received in his laboratory and for the many valuable discussions.

Thanks are also due to the staff members of the S.T.K. in Mol and more particularly to Dr. M. D'HONT and Dr. NÈVE DE MÉVERGNIES.

We are also grateful to Dr. W. ORR who corrected the English manuscript.

SUMMARY

A method has been developed for the determination of vanadium in high alloy steels by radioactivation analysis. Manganese present in the steel sample is used as an internal standard, thus permitting accurate correction of neutron flux irregularities between sample and reference. The method was tested on 4 National Bureau of Standard samples having a vanadium content from 0.014 up to 2.04% and a widely differing composition as regards other alloy constituents. The results obtained by radioactivation in the Belgian Reactor BR1 and the Amsterdam 28 MeV deuteron cyclotron show satisfactory accuracy as well as precision.

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Received October 14th, 1957

Short Communication

Dosage colorimétrique du fer par l'α-α'-dipyridyle

Dans une étude précédente[1] nous avons montré l'influence inhibitrice du cation Zn^{+2} sur le développement de la teinte donnée par le cation Fe^{+2} avec l'α-α'-dipyridyle.

Nous avons pensé que la présence d'autres cations pouvait devenir gênante pour le dosage colorimétrique du fer, et nous avons étudié, tout d'abord, l'influence des cations:

$$Co^{+2}, Ni^{+2}, Mn^{+2}$$

dans ce dosage.

Nous avons reconnu ques ces cations présentent la même action inhibitrice que Zn^{+2}.

Une série d'essais systématiques ont été effectués:
À un volume constant d'une solution titrant 10 γ/ml de Fe^{+3} nous ajoutons des volumes croissants de solutions titrées à 100 γ/ml de Co^{+2}, Ni^{+2} et Mn^{+2}.

Nous avons constaté que la méthode[2] reste applicable tant que le rapport: $\frac{M^{+2}}{Fe^{+2}}$ n'excède pas:

15 pour le cobalt,
22 pour le nickel,
80 pour le manganèse.

Les mêmes valeurs ont été trouvées en utilisant des solutions de chlorures, de sulfates et d'acétates de ces métaux.

Dans tous les cas, nous avons constaté qu'aux concentrations en Fe^{+2}, auxquelles la méthode est applicable, la coloration propre à chacun des 3 cations n'intervient pas.

Faculté des Sciences, Toulouse (France) M. Grat-Cabanac

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Reçu le 15 mars 1958

SEPARATION OF RHODIUM AND IRIDIUM BY MULTIPLE FRACTIONAL EXTRACTION

by

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In other work BERG AND SENN[1] determined the distribution coefficients of the chloro complexes of rhodium and iridium in a hydrochloric acid-tributyl phosphate system. The distribution coefficients were sufficiently different to suggest a resolution by multiple solvent extraction. Attempts to resolve mixtures of the two metals by countercurrent extraction failed because it was necessary to oxidize the iridium remaining in the original raffinate after each extraction.

Therefore it was necessary to use a multiple extraction technique that would permit repeated oxidation of the original raffinate phase. The method of BUSH AND DENSEN[2] appeared completely suited to the problem since nine equilibrations theoretically would effect a practical resolution of the two noble metals.

EXPERIMENTAL

Apparatus

Beckman Model DU spectrophotometer with matched 1.000 cm quartz cells. Nine small separatory funnels.

Reagents

Stock solutions of the precious metals were prepared by dissolving respectively rhodium(III) chloride and iridium(IV) chloride (A. D. Mackay, Inc.) in 100 ml of concentrated hydrochloric acid. The solutions were diluted to 1 l with distilled water and standardized by spectrophotometric procedures. The rhodium solution was standardized by the method of AYRES AND YOUNG[3]. The iridium solution was standardized by the method of AYRES AND QUICK[4]. Standards for the spectrophotometric working curves were verified by the gravimetric procedures devised by GILCHRIST[5].

All other chemicals used were reagent grade.

Measurement of distribution coefficients

The procedure followed for measuring the distribution coefficients of the chloro complexes of rhodium and iridium is described below.

Six 5.00-ml aliquots of each stock sample solution were taken to dryness on a steam bath. The samples were then dissolved in appropriate amounts of concentrated hydrochloric acid such that on dilution to 15 ml the molar concentration of the acid in the six samples was 1, 2, 3, 5, 7, and 9. The systems then were saturated with sodium chloride and equilibrated with 10 ml of tributyl phosphate.

The raffinate was filtered through Whatman No. 1 filter paper. This eliminated the contamination of the raffinate by the tributyl phosphate, because the extractant would not pass through the wet filter paper. The raffinate was then analyzed for the appropriate metal.

Aqua regia was added to each sample before it was evaporated to a moist residue. The residues then were dissolved in concentrated hydrochloric acid and again evaporated nearly to dryness. Residues containing rhodium were dissolved in 3% hydrochloric acid and the rhodium content was determined by the spectrophotometric procedure of AYRES AND YOUNG[3]. Residues containing iridium were dissolved in 10% hydrochloric acid and the iridium content was determined by the spectrophotometric procedure of AYRES AND QUICK[4]. The data collected in these experiments may be seen in Tables I and II.

TABLE I

EXTRACTION OF RHODIUM FROM HYDROCHLORIC ACID–SODIUM CHLORIDE SYSTEMS WITH TRIBUTYL PHOSPHATE

HCl concentration (M)	*mg Rh taken*	*mg Rh in raffinate*	*mg Rh in extractant*	*K_d
1	3.70	3.70	0.00	0.00
3	3.70	3.35	0.35	0.16
5	3.70	3.11	0.59	0.29
7	3.70	3.11	0.59	0.29
9	3.70	3.11	0.59	0.29

$$* \; K_d = \frac{\text{mg Rh/ml of extractant}}{\text{mg Rh/ml of raffinate}}$$

TABLE II

EXTRACTION OF IRIDIUM FROM HYDROCHLORIC ACID–SODIUM CHLORIDE SYSTEMS WITH TRIBUTYL PHOSPHATE

HCl concentration (M)	*mg Ir taken*	*mg Ir in raffinate*	*mg Ir in extractant*	*K_d
1	2.66	2.36	0.30	0.19
2	2.66	1.39	1.27	1.37
3	2.66	1.36	1.30	1.43
5	2.66	0.79	1.87	3.53
7	2.66	0.72	1.94	4.04
9	2.66	0.89	1.77	3.00

$$* \; K_d = \frac{\text{mg Ir/ml of extractant}}{\text{mg Ir/ml of raffinate}}$$

Extraction technique

The extraction technique used for the separation of rhodium and iridium is that of BUSH AND DENSEN[2]. Since it is not encountered too frequently in analytical work, some discussion of the technique is necessary.

Let XI_0 and YI_0 represent the initial portion of the organic phase and aqueous phase respectively. After the solute a has distributed itself between the two phases and equilibrium is attained, the phases are separated into raffinate, XI_1, and extractant, YI_1. Multiple fractional extraction is achieved by introducing fresh portions of the two solvents, YII_0 and XII_0, which are added to the original raffinate and extractant respectively. The various combinations, equilibrations, and separations of phases are carried out according to the extraction pattern given in Fig. 1. Subscripts denote the number of extractions the solution has passed through.

The fraction of solute a found in the raffinate phase after the first equilibration is designated by P_a. The fraction of solute transferred to the extractant must equal $(1 - P_a)$ or Q_a. The value of P_a may be determined in the following manner.

If V_x and V_y equals the total volume of raffinate and extractant respectively, then;

$$\text{the total amount of } a \text{ in } XI_1 = (\text{mg of } a/\text{ml } XI_1)\, V_x$$

and

$$\text{the total amount of } a \text{ in } YI_1 = (\text{mg of } a/\text{ml } YI_1)\, V_y$$

$$\frac{P_a}{1 - P_a} = \frac{(\text{mg of } a/\text{ml } XI_1)\; V_x}{(\text{mg of } a/\text{ml } YI_1)\; V_y} = K_a \frac{V_x}{V_y}$$

By transposing and combining terms

$$P_a = \frac{K_a\, V_x}{K_a\, V_x + V_y},$$

where K_a is the distribution coefficient of the solute. Perhaps it should be noted at this point that K_a is the reciprocal of K_d as defined in Tables I and II.

The greatest fractional separation of several solutes is achieved if the same fraction of *a* is found in XI_1, as of *b* in YI_1. That is when $P_a = Q_b = 1 - P_b$, or

$$\frac{K_a V_x}{K_a V_x + V_y} = 1 - \frac{K_b V_x}{K_b V_x + V_y}$$

This expression can be simplified to show that the greatest fractional separation is attained if

$$\frac{V_x}{V_y} = \sqrt{\frac{1}{K_a K_b}}$$

The volume ratio of 14 ml extractant to 15 ml raffinate used in the experimental procedure is based on this equation.

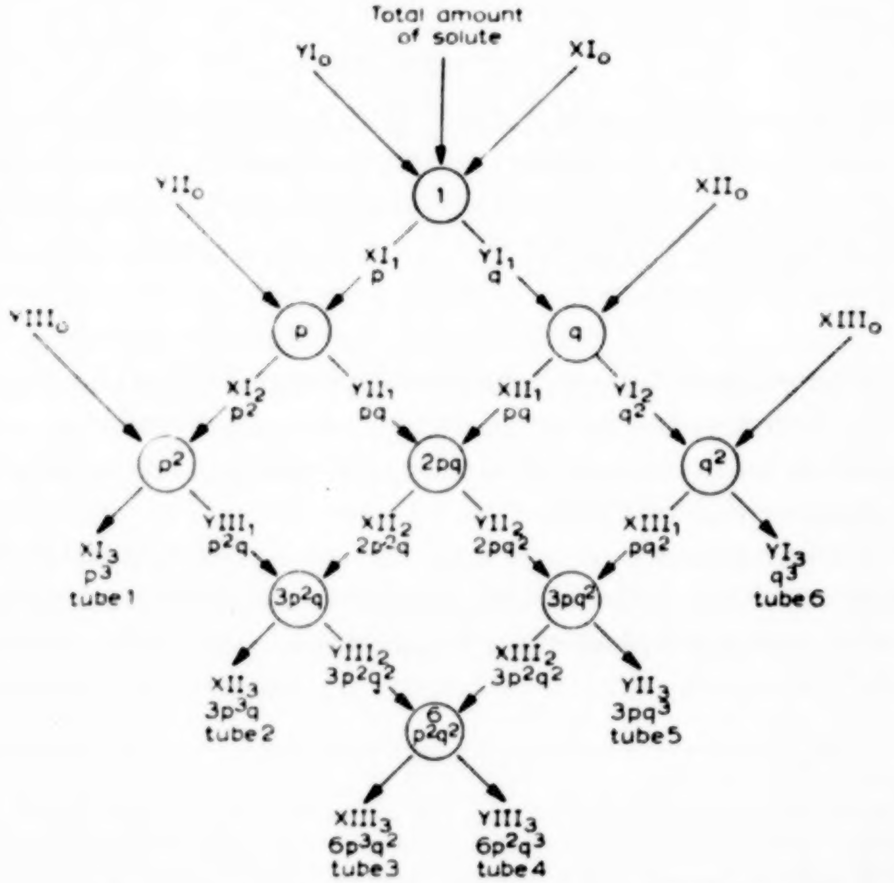
Total amount of solute
YI₀
XI₀
1
YII₀
XII₀
XI₁ p
YI₁ q
YIII₀
p
q
XIII₀
XI₂ p²
YII₁ pq
XII₁ pq
YI₂ q²
p²
2pq
q²
XI₃ p³ tube 1
YIII₁ p²q
XII₂ 2p²q
YII₂ 2pq²
XIII₁ pq²
YI₃ q³ tube 6
3p²q
3pq²
XII₃ 3p³q tube 2
YIII₂ 3p²q²
XIII₂ 3p²q²
YII₃ 3pq³ tube 5
6 p²q²
XIII₃ 6p³q² tube 3
YIII₃ 6p²q³ tube 4

Fig. 1. Extraction pattern of BUSH AND DENSEN[2].

The algebraic calculation of the fraction of solute found in each phase is shown in Fig. 1. The circled terms represent the fractional amount of a single solute found in that particular heterogenous system. Whereas the composition of any single phase is given below the appropriate circle in terms of *p* and *q*. For example, the composition of the raffinate which is collected in tube 1 is given by the term p^3 since the solute *a* has been partitioned between the solvents on three occasions. Ultimately, the solute concentrated in the raffinate phase appears in tubes 1, 2, and 3. The solute concentrated in the extractant appears in tubes 4, 5, and 6.

Separation of rhodium and iridium

The sample containing the mixture of rhodium and iridium was evaporated to dryness on a steam bath. The residue was then dissolved in 6*N* hydrochloric acid saturated with sodium chloride. One ml of hydrogen peroxide was added and the solution boiled vigorously. The sample solution was cooled, transferred to a separatory funnel and diluted to 15 ml with the hydrochloric acid–sodium chloride mixture. The sample solution was then equilibrated with 14 ml of tributyl phosphate. The extractions were carried out using the extraction pattern of BUSH AND DENSEN[2]. However, the original raffinate had to be oxidized with hydrogen peroxide each time it was extracted in order to completely remove the iridium. This means that raffinate solutions XI_0, XI_1 and XI_2 had to be oxidized before being contacted by extractant solutions YI_0, YII_0, and $YIII_0$. No further oxidations were needed after the three mentioned above had been accomplished.

The extractant phase was stripped by equilibrating with 15 ml of a 25% nitric acid solution saturated with sodium nitrate. Usually three to five equilibrations were sufficient to quantitatively remove any rhodium or iridium from the extractant. The analyses were carried out by the methods described above.

TABLE III

DATA FOR THE SEPARATION OF RHODIUM AND IRIDIUM

System: hydrochloric acid–sodium chloride–tributyl phosphate
Quantities taken: 2.66 mg of iridium and 3.70 mg of rhodium

Tube No.	*Run No. 1*		*Run No. 2*		*Run No. 3*		*Run No. 4*	
	mg Rh	*mg Ir*	*mg Rh*	*mg Ir*	*mg Ir*	*mg Ir*	*mg Rh*	*mg Ir*
1	3.35	0.00	3.56	0.00	3.66	0.00	3.56	0.00
2	0.20	0.00	0.10	0.00	tr	0.00	0.19	0.00
3	tr	0.00	tr	0.00	0.00	0.00	0.00	0.00
4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00	0.35	0.00	0.31	0.00	0.31	0.00	0.39
6	0.00	2.20	0.00	2.14	0.00	2.20	0.00	2.15

Average recovery of rhodium = 3.66 mg
Average recovery of iridium = 2.51 mg

The results obtained from four separations appear in Table III. 99% of the rhodium and 94% of the iridium are recovered free of the other metal in 9 equilibrations. Complete resolution and recovery of each metal would not be expected unless more equilibration steps were introduced.

Theoretical considerations envisage a symmetrical distribution of the two solutes. The predicted distribution of the solutes is given in Table IV. In Fig. 2 the theoretical and experimental values are plotted for comparison.

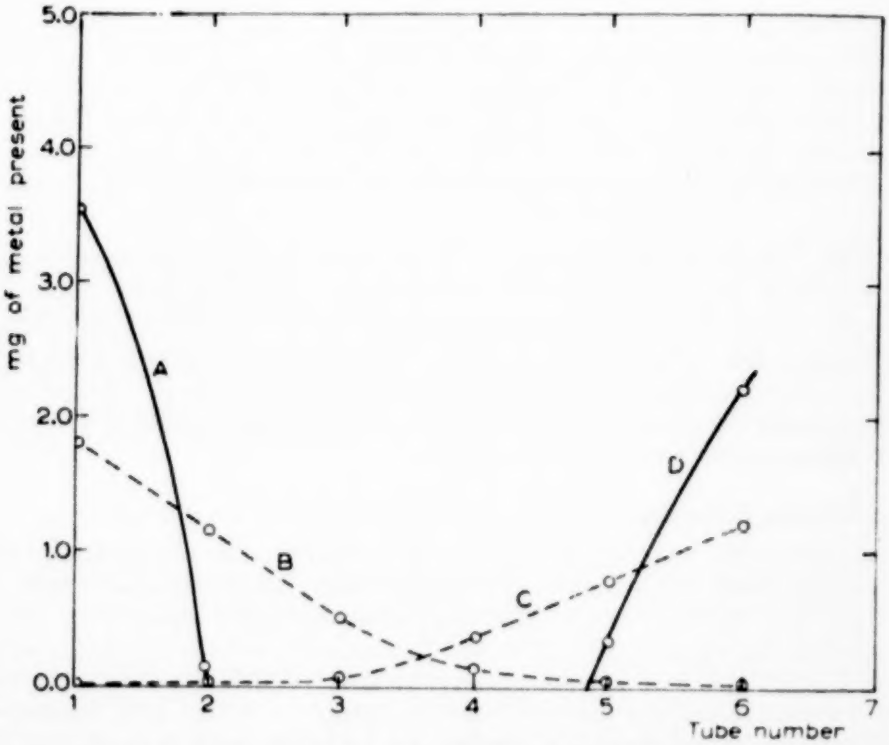

Fig. 2. Distribution curves for the separation of rhodium and iridium
A– Experimental rhodium curve C– Theoretical iridium curve
B– Theoretical rhodium curve D– Experimental iridium curve

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TABLE IV

THEORETICAL DATA FOR THE SEPARATION OF RHODIUM AND IRIDIUM

Tube No.	*Fraction of Rh present*	**mg Rh present*	*Fraction of Ir present*	**mg Ir present*
1	0.49	1.81	0.01	0.027
2	0.31	1.15	0.025	0.066
3	0.13	0.48	0.039	0.10
4	0.036	0.15	0.14	0.37
5	0.023	0.074	0.31	0.82
6	0.01	0.037	0.47	1.25

* Based on 2.66 mg of iridium and 3.70 mg of rhodium taken for separation

DISCUSSION

Theoretical considerations are greatly simplified if a few assumptions are made. First, one must assume that the distribution coefficient does not vary with concentration and that the solute is not appreciably associated or dissociated in either phase. Second, there must be negligible adsorption of the solute on the apparatus or at the liquid-liquid interface. In dealing with mixtures of solutes, it must also be assumed that each solute is distributed independently of the other.

It was on these assumptions that the theoretical distribution curves were calculated. Obviously, these assumptions are not true in a non-ideal system, but the deviations must be determined experimentally since there is no method for calculating all of the interactions. Probably the poorest assumption was the first. Nevertheless, reasonable agreement was observed between the theoretical and experimental results.

Although the oxidation step required before each extraction of the original raffinate was time consuming, the separation was easily completed in 1-1$^1/_2$ h. It is not known why the iridium must be oxidized in successive steps to complete the extraction.

SUMMARY

Mixtures of the chloro complexes of rhodium(III) and iridium(IV) were resolved by a nine stage multiple extraction technique. The solutes are partitioned in a hydrochloric acid - tributyl phosphate system. Rhodium is concentrated in the raffinate while iridium is concentrated in the extractant. 99% of the rhodium and 94% of the iridium are recovered free of the other metal. Experimental results agree reasonably well with the results predicted by a theoretical treatment of the distribution data.

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Received November 11th, 1957

THE GRAVIMETRIC DETERMINATION OF TUNGSTEN IN THE PRESENCE OF MOLYBDENUM

by

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INTRODUCTION

In a previous investigation of the gravimetric methods for the determination of tungsten[1], cinchonine and β-naphthoquinoline have been recommended, as they are the only reagents giving an error less than 0.1%. As several authors mention a strong coprecipitation of Mo in the classical WO_3 precipitation with inorganic acids, it will be of interest to investigate the behaviour of these reagents when used for the tungsten determination in W-Mo mixtures, in order to work out a gravimetric method with negligible coprecipitation.

PRECIPITATION WITH ORGANIC REAGENTS

Experimental

Solutions

The Na_2WO_4 solution was analysed by the Berzelius method, using $Hg_2(NO_3)_2$ in slightly ammoniacal medium.

An approximately 10% Mo stock solution was made by dissolving 25.25 g of $Na_2MoO_4 \cdot 2\,H_2O$ in 100 ml of water.

Mixtures containing 25 ml of Na_2WO_4 solution and different amounts of Na_2MoO_4 solution were used for the analyses.

Precipitation with cinchonine

Procedure. 15 ml of concentrated HCl are added and drop by drop while stirring, to the Mo-W mixture, which is then heated to the boiling point. Some filter pulp is added, and the hot solution treated with a few drops of conc. HNO_3 and 4 ml of the reagent solution (12.5 g cinchonine in 100 ml $6N$ HCl), after which it is heated again for 5 min.

After digestion for 1 h on the steam bath, the hot solution is filtered, and the precipitate washed with a hot 1:30 dilute reagent solution. The precipitate is ignited at 850°. For results see Table I.

Precipitation with β-naphthoquinoline

Procedure. To the cold W-Mo mixture, 15 ml of conc. HCl are added drop by drop, while stirring, followed by a few drops of conc. HNO_3. The solution is heated to the boiling point, some filter pulp and 4 ml of the reagent solution (2 g of β-naphthoquinoline in $1.4N$ HNO_3) are added. After digestion for 1 h on a steam bath, the hot solution is filtered, and the precipitate washed with a hot dilute reagent solution (5 ml reagent solution + 95 ml $0.2N$ HNO_3). The precipitate is ignited at 850°. For results see Table I.

Discussion

Both reagents, although excellent for the determination of W in pure tungstate solutions, cannot be used directly in the presence of Mo, as they give results which are too high owing to the coprecipitation and adsorption of MoO_3. Therefore, a study of the methods that can be used in order to minimize the coprecipitation, is needed.

TABLE I

Mo/W	With cinchonine			With β-naphthoquinoline		
	mg ↓	mg ↓ MoO_3	% error in WO_3*	mg ↓	mg ↓ MoO_3	% error in WO_3*
2	429.6	114.2	+36.2	405.6	90.2	+28.6
1	390.7	75.3	+24.0	368.1	52.7	+16.7
0.4	361.5	46.1	+14.6	348.6	33.2	+10.5
0.2	345.4	30.0	+ 9.5	338.8	23.4	+ 7.4
0.1	333.6	18.2	+ 5.8	330.7	15.3	+ 4.9
0.04	326.2	10.8	+ 3.4	323.3	7.9	+ 2.5
0	315.2		− 0.06	315.1	—	− 0.1

* Theoretical amount: 315.4 mg WO_3

REDUCTION OF COPRECIPITATION

Survey of the methods

In the method of SCHNEIDER[2] the mixture of WO_3 and MoO_3 is purified by heating it to a high temperature, in order to eliminate the volatile MoO_3. This method, however, does not give quantitative results. The method of ROSE[3], using tartaric acid and H_2S, as well as the method in which Mo is volatilized as oxychloride in a dry HCl-stream[4,5], cannot be used as practical analytical methods[6].

Freshly precipitated molybdic acid seems to be soluble in mineral acids in contrast to the insoluble tungstic acid[7]. Consequently warm conc. H_2SO_4 was used by DESI[8] and RUEGENBERG *et al.*[9], and later again by HOMMEL[6], who reported good results with a modified method.

Experimental

Before using one of these methods for the determination of W in Mo-W mixtures, preliminary tests were made with pure tungstate solutions, to ascertain whether the methods can be used quantitatively.

Mineral acids

With tungstate solutions

Procedure. The precipitation of WO_3 was carried out in the usual way, with a cinchonine reagent solution. The precipitate and filter were treated in a beaker with 20 ml of acid, boiled for 5 min, washed with dilute mineral acid and ignited at 850°. Experiments were also performed in which the treatment with acid was carried out twice. For results see Table II.

TABLE II

Acid	Treated once		Treated twice	
	mg ↓	% error in WO_3	mg ↓	% error in WO_3
12*N* HCl	314.6	−0.25	313.8	−0.51
14*N* HNO_3	315.3	−0.03	315.1	−0.10
10*N* H_2SO_4	313.9	−0.48	313.4	−0.63

With mixtures

If this treatment is used for W-Mo mixtures, a slight decrease of the coprecipitation is obtained. However, the errors are too high, clearly indicating that coprecipitated Mo cannot be separated from WO_3, even by treating twice with mineral acids. This agrees with the results obtained by VON HEVESY[10] in the case of a Mo-Fe-Al separation.

Concentrated sulfuric acid

Preliminary centrifuge method

A treatment of the precipitate with conc. H_2SO_4 does not allow the use of filter paper or filter pulp. Therefore a centrifuge method was worked out first, in which the precipitate, formed in the presence of cinchonine, was centrifuged, washed and dissolved in 5 ml of NH_4OH. The solution was transferred quantitatively to a weighed crucible, slowly evaporated, dried and ignited at 850°.

The results of 282.6; 282.3; 282.7 and 282.1, instead of 282.7 mg WO_3 do not indicate a loss by this method, which can be used with the sulfuric acid treatment.

With tungstate solutions

Procedure. Precipitation using cinchonine is carried out as indicated above. The WO_3 is centrifuged, washed with a dilute cinchonine solution (1 : 30), treated with 4 ml of conc. H_2SO_4 and a few drops of conc. HNO_3, and heated. After cooling, 12 ml of water are added and the solution is centrifuged again. This treatment is repeated a second time, and the precipitate dissolved in ammonia and ignited at 850°, as already mentioned.

The results of 281.9; 282.1; 282.2 and 282.4 mg instead of 282.7 mg WO_3, with a mean error of 0.18% with respect to the reference method do not indicate an appreciable loss.

With mixtures

On applying this method to precipitates from Mo–W mixtures, the following results were obtained.

TABLE III

Mo/W	*Treated once*			*Treated twice*		
	mg ↓	*mg* ↓ *MoO_3*	*%error in WO_3**	*mg* ↓	*mg* ↓ *MoO_3*	*%error in WO_3**
2	333.2	50.5	+17.9	304.7	22.0	+7.8
1	325.6	42.9	+15.2	300.3	17.6	+6.2
0.4	307.5	24.8	+ 8.8	294.2	11.5	+4.1
0.1	290.8	8.1	+ 2.9	286.0	3.3	+1.2
0.04	286.0	3.3	+ 1.2	284.3	1.6	+0.6

* Theoretical amount: 282.7 mg WO_3

Discussion

The results indicate that only a negligible amount of the WO_3 precipitate is lost when it is treated with mineral acid, or with concentrated sulfuric acid. Although the contamination of the WO_3 precipitate is reduced by treating it twice with conc. H_2SO_4, the errors still remain too high and do not allow a direct gravimetric determination. However, this treatment with mineral acids will be used in the following reprecipitation method.

REPRECIPITATION METHOD

As none of the methods mentioned can be used successfully for a direct gravimetric determination of W in the presence of Mo, owing to coprecipitation phenomena and the lack of procedures for eliminating the MoO_3, reprecipitation seems to be indicated.

In this method, β-naphthoquinoline, which gives smaller coprecipitation errors than cinchonine, will be used as reagent, in the presence of H_2O_2.

The precipitate is treated with mineral acids, dissolved in NaOH and reprecipitated from alkaline solutions. In order to make sure that no loss occurs in these different steps, they were all worked out first with pure tungstate solutions.

Experimental

Preliminary experiments

As it is unnecessary to review the procedures of these steps *in extenso*, only a survey of the results will be given, obtained by using in each case 25 ml tungstate solution with a content of 172.1 mg WO_3 (reference method).

Treatment with HNO_3. The precipate, formed in the presence of β-naphthoquinoline, is treated with 14*N* HNO_3, and filtered again in the usual way.

No loss is indicated by the results of 171.7; 171.9 and 172.0 mg WO_3.

Precipitation from alkaline solution. After treatment with HNO_3 the precipitate is dissolved in NaOH. This solution is acidified, β-naphthoquinoline is added and the precipitate again treated with HNO_3 before filtration.

The results of 171.4; 171.6; 171.7 and 172.0 with a mean error of 0.25% with respect to the real value, are satisfactory.

Use of H_2O_2. All the precipitations are carried out in the presence of H_2O_2: treatment with HNO_3 and reprecipitation are performed in the usual way.

The results are 171.2; 171.4; 171.5 and 172.0 with a mean error of 0.34% with regard to the true value.

Final method

The method chosen for mixtures is as follows:

To 25 ml of the cold solution are added: 10 ml conc. HCl, a few drops of conc. HNO_3, 2 ml of perhydrol and filter pulp. The solution is heated to the boiling point, treated with 3 ml of reagent solution (2 g of β-naphthoquinoline and 10 ml 14*N* HNO_3 to 100 ml), and digested on a hot steam-bath. The clear supernatant liquid is poured through a filter paper, which is then added to the original precipitate. This is treated with 15 ml of water, 6 ml of 14*N* HNO_3, 2 ml of perhydrol and 3 ml of reagent solution. After heating and digesting, it is filtered. Filter paper and precipitate are treated in a beaker with 30 ml of 5% NaOH, heated on a steam bath, and diluted with 30 ml of warm water. The hot Na tungstate solution is filtered, and the filter washed three times with dilute NaOH (0.1%). The solution and washing liquids are evaporated slowly on a sand bath to 50 ml, and treated with 3 ml of perhydrol. After heating to the boiling point, 20 ml of conc. HCl, 1 ml of 14*N* HNO_3 and 8 ml of reagent solution are added. After digestion on a steam bath, the clear supernatant liquid is poured through a filter, which is added to the precipitate in the beaker, and treated again with 15 ml of H_2O, 6 ml of 14*N* HNO_3, 2 ml of perhydrol and 3 ml of reagent solution.

After heating to the boiling point and digesting, the precipitate is filtered, washed with a dilute reagent solution (5 ml + 95 ml 0.2*N* HNO_3), dried and ignited at 850°.

With mixtures

Using this reprecipitation method for W–Mo mixtures, the following results were obtained.

TABLE IV

Mo/W	*mg* ↓	*mg* ↓ *MoO_3*	*% error in WO_3*
2	174.3	2.2	+1.28
0.8	173.9	1.8	+1.04
0.4	173.1	1.0	+0.58
0.16	172.4	0.3	+0.17

Discussion

These results clearly indicate a great improvement compared with the results obtained with β-naphthoquinoline alone. The coprecipitation phenomena can be diminished by the reprecipitation method, combined with a treatment with HNO_3, using β-naphthoquinoline as reagent, in the presence of H_2O_2.

SUMMARY

β-Naphthoquinoline and cinchonine, though excellent for the gravimetric determination of W, are not satisfactory when Mo is present in the solution.

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Treatment of the precipitate with mineral acids, especially with sulfuric acid, was studied: only a slight decrease of the coprecipitation phenomena was observed. A reprecipitation method was developed, which involved the use of β-naphthoquinoline as reagent in the presence of H_2O_2 and treatment of the precipitate with HNO_3. The error is 0.6% for a Mo/W ratio = ½ and becomes slightly higher than 1% for Mo/W = 1.

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Received November 11th, 1957

THE ANALYSIS OF SOLUTIONS CONTAINING MIXTURES OF LINEAR SODIUM PHOSPHATES

by

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The analysis of phosphate mixtures has long been a difficult problem. Phosphates and polyphosphates in aqueous solution, yield complex equilibria which are difficult to interpret and to analyze quantitatively.

Important analytical contributions have been made by Bell[1], Gerber and Miles[2], and Jones[3]. Raistrick, Harris and Lowe[4] have reported a procedure for the analysis of commercial sodium triphosphate. The current investigation has resulted in the development of a new method of analysis for sodium ortho-, pyro-, and triphosphate when only these three linear phosphates are present in aqueous solution.

This procedure for analysis has been tested by application to a representative series of synthetic mixtures also subjected to analyses by the Bell method. The new analysis consisted of the following experimental steps:

(1) In the pH range 4.0–4.5 zinc pyrophosphate was reprecipitated from a measured aliquot at 19°.

(2) Standard silver nitrate solution was titrated conductometrically at 12° with phosphate mixtures.

(3) After complete hydrolysis in hot acid solutions, total phosphate was determined by the magnesia method[5,6].

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Each step in the procedure was represented in common terms, *i.e.*, moles P_2O_5, by an algebraic equation:

$$p = K = \frac{(\text{wt. } Zn_2P_2O_7)\ (\text{total sample volume})}{(\text{mol. wt. } Zn_2P_2O_7)\ (\text{aliquot volume})} = \text{moles } P_2O_5\ . \quad . \quad . \qquad (1)$$

$$90 + 6p + 5t = 3/2\, L = \frac{3\ (\text{vol. } Ag^+)\ (\text{moles } Ag^+/\text{ml})\ (\text{total sample volume})}{2\ (\text{volume of phosphate mixture used in titration})} = \text{moles } P_2O_5\ . \quad . \qquad (2)$$

$$o + p + t = M = \frac{(\text{wt. } Mg_2P_2O_7)\ (\text{total sample volume})}{(\text{molecular wt. } Mg_2P_2O_7)\ (\text{aliquot vol.})} = \text{moles } P_2O_5\ . \qquad (3)$$

wherein:
o = moles of P_2O_5 derived from moles of Na_3PO_4 present in the mixture.
p = moles of P_2O_5 derived from moles of $Na_4P_2O_7$ present in the mixture.
t = moles of P_2O_5 derived from moles of $Na_5P_2O_{10}$ present in the mixture.

A simultaneous solution of these three equations containing three unknowns yields:

$$p = K\ . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

$$o = \frac{3L - 2K - 10M}{8} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

$$t = \frac{18M - 6K - 3L}{8} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Incorporation of molecular weights and conversion factors in equations resulted in the following:

$$\%\ Na_3PO_4 = \frac{[(122.978\ L - (81.985\ K) - (409.675\ M)]\ (100)}{\text{total sample weight}} \quad . \quad . \qquad (7)$$

$$\%\ Na_4P_2O_7 = \frac{(266.03\ K)\ (100)}{\text{total sample weight}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

$$\%\ Na_5P_3O_{10} = \frac{[(551.895 M) - (183.965\ K) - (91.983\ L)]\ (100)}{\text{total sample weight}} \quad . \quad . \qquad (9)$$

Theoretical values for K were calculated from the introduced composition and the expression:

$$K = \frac{\text{introduced weight of } Na_4P_2O_7}{\text{molecular weight of } Na_4P_2O_7} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

Experimental and theoretical values of K were compared. The average deviation of percentage error in K was found to be 4.43%.

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The quantity L was measured for each mixture by titrating conductometrically, at 12°, standard silver nitrate with the phosphate solutions. In a mixture of ortho-, pyro-, triphosphate, each mole of orthophosphate, PO_4^{-3}, will require three moles of silver ion, each mole of pyrophosphate, $P_2O_7^{-4}$ will require four moles of silver ion, and each mole of triphosphate $P_3O_{10}^{-5}$ will require five moles of silver ion. Thus L represented the total number of moles of silver ion, equivalent to the phosphates in solution.

Theoretically L was calculated from the following expression:

$$L = (3)\,(\text{moles } PO_4^{-3}) + (4)\,(\text{moles } P_2O_7^{-4}) + (5)\,(\text{moles } P_3O_{10}^{-5}) \quad . \quad . \ (11)$$

The average deviation from theory of the percentage errors for L was 1.39%.

After hydrolysis in hot hydrochloric and nitric acid solution, the reprecipitation of magnesium ammonium orthophosphate followed by ignition to magnesium pyrophosphate permitted determination of total pyrophosphate and the quantity M, *i.e.*, the total phosphate determination expressed as moles P_2O_5. A theoretical value for M was calculated by making a summation of the moles of the individual components of a given synthetic mixture expressing each as moles of P_2O_5.

$$M = \frac{1}{2}\text{ moles } PO_4^{-3} + \text{moles } P_2O_7^{-4} + \frac{3}{2}\text{ moles } P_3O_{10}^{-5} \quad . \quad . \quad . \ (12)$$

Comparative data have shown an average deviation of percentage error of theory of 2.5%.

Analytical data resulting from applications of the new procedure and the **Bell** method to aqueous linear phosphate mixtures of known composition are summarized

TABLE I

COMPARITIVE ANALYTICAL DATA - AQUEOUS LINEAR PHOSPHATE MIXTURES

Introduced composition			*Simultaneous analysis*			*Bell analysis*		
Wt.% Na_3PO_4	*Wt.% $Na_4P_2O_7$*	*Wt.% $Na_5P_3O_{10}$*	*Wt.% Na_3PO_4*	*Wt.% $Na_4P_2O_7$*	*Wt.% $Na_5P_3O_{10}$*	*Wt.% Na_3PO_4*	*Wt.% $Na_4P_2O_7$*	*Wt.% $Na_5P_3O_{10}$*
100.00	0.00	0.00	98.7	0.00	3.1	95.17	0.00	0.00
100.00	0.00	0.00	98.6	0.0	3.3			
50.00	0.00	50.00	46.0	0.0	55.3	55.04	0.00	43.45
50.00	0.00	50.00	48.8	0.0	53.2			
0.00	0.00	100.00	3.4	0.0	98.1	0.00	0.00	104.23
0.00	0.00	100.00	5.1	0.0	96.8			
33.30	33.30	33.40	39.9	33.9	27.7	30.64	34.94	32.85
33.30	33.30	33.40	39.3	33.7	27.8			
50.00	50.00	0.00	46.2	48.9	4.5	44.48	48.49	4.20
50.00	50.00	0.00	51.2	45.9	3.5			
0.00	50.00	50.00	0.0	53.2	53.8	5.50	55.91	39.68
0.00	50.00	50.00	0.00	52.4	55.8			
20.93	58.14	20.93	22.9	58.7	18.4	0.04	61.75	13.18
20.93	58.14	20.93	21.8	58.7	19.2			
0.00	100.00	0.00	0.0	97.2	8.3	0.00	99.65	0.00
0.00	100.00	0.00	0.0	95.1	11.6			

in Table I. Examination of those data has disclosed that the new analyses were more accurate than those obtained by the BELL procedure in the majority of cases. Furthermore, this new analytical method permits reasonable accuracy for determination of ortho-, pyro-, and triphosphate present in aqueous mixtures provided that no foreign ions are present which will interfere with the conductance titration of silver nitrate.

EXPERIMENTAL

Preparation of pure sodium phosphates

Commercially available sodium triphosphate was purified for use in analytical studies. A saturated solution of commercial sodium triphosphate was subjected to vacuum distillation of moisture at room temperature. After approximately three-fourths of the water had been removed, the recrystallized product was collected, dried in air and subjected to complete hydrolysis followed by an analysis for total phosphate. Theory dictated that the recrystallized product should contain 77.3% $Na_5P_3O_{10}$ and 22.7% water as water of hydration. Its composition was calculated from total phosphate and moisture analyses to be 77.6% $Na_5P_3O_{10}$ and 22.9% water. A solution of the recrystallized product gave no precipitate with zinc in the pH range 3.8 – 4.5, neither was a blue obtained upon treatment with acidified ammonium molybdate and 1,2,4-aminonaphtholsulfonic acid in the presence of sodium bisulfite.

Reagent-grade trisodium orthophosphate and tetrasodium pyrophosphates were checked for purity by an analysis for total phosphate.

Preparation of synthetic mixtures for analysis

The relative proportions of ortho-, pyro-, and triphosphates in a given mixture are believed to influence the results obtained for determination of triphosphate by selective precipitation of zinc pyrophosphate[7]. For this reason the compositions of the synthetic mixtures to be analyzed were chosen from a three-coordinate plot of possible compositions. Such a plot permitted selection of mixtures which might best represent all compositions. The preparation of solutions for analysis is summarized in Table II.

TABLE II

COMPOSITION OF SYNTHETIC MIXTURES

Sample	*Sample at final volume*	Na_3PO_4		$Na_4P_2O_7$		$Na_5P_3O_{10}$			*Total weight phosphates*
		Wt. g	*Wt. %*	*Wt. g*	*Wt. %*	*Wt.* $Na_5P_3O_{10}\cdot 6H_2O$ *g*	*Wt.* $Na_5P_3O_{10}$ *g*	*Wt. %*	
1	200.00	1.7332	100.00	—	—	—	—	—	1.7332
2	200.00	1.7332	50.00	—	—	2.2418	1.7332	50.00	3.4664
3	250.00	—	—	—	—	4.0002	3.0926	100.00	3.0926
4	250.00	2.0704	33.30	2.0704	33.30	2.6855	2.0762	33.40	6.2170
5	200.00	2.0704	50.00	2.0704	50.00	—	—	—	4.1408
6	200.00	—	—	2.5650	50.00	3.3178	2.5650	50.00	5.1300
7	250.00	1.2066	20.93	3.3520	58.14	1.5606	1.2065	20.93	5.7651
8	200.00	—	—	5.1300	100.00	—	—	—	5.1300

The precipitation of zinc pyrophosphate at 19°

A measured aliquot containing 0.2 or 0.3 g dissolved solids of a given synthetic unknown was withdrawn, diluted to 100 ml, and adjusted to pH 4.0 – 4.5 with dilute hydrochloric acid. The resulting solution was permitted to come to temperature in a 400-ml beaker immersed in a water bath at 19°. 70 ml of an approximately 0.2*M* solution of zinc sulfate were added with continous stirring and agitation continued for 5 min. The pH of this mixture was readjusted to 4.0 – 4.5 with dilute sodium hydroxide and the sample removed from the water bath, and allowed to stand for periods of 15 to 45 min (15 min was the recommended period[1]). The precipitate was removed upon No. 40 Whatman filter paper and washed with 150 ml of distilled water. (Ice cold distilled water is recommended.) A hole was made in the apex of the filter paper, the precipitate washed into a clean beaker with distilled water, and dissolved in dilute hydrochloric acid, about 5 ml of approximately 1*N* HCl. 25 ml of zinc sulfate solution were added after the acid solution had reached 19°. The pH was again adjusted to 4.0 – 4.5. The mixture was removed from the water bath and allowed to stand for 15 – 45 min (15 min was recommended). The precipitate was removed, treated as before, placed in a weighed porcelain crucible and ignited gradually from 25° to 940° in an electric muffle furnace. A peak temperature of 900 – 940° was recommended. The crucible and its contents were allowed to cool and were weighed.

Conductance titrations at 12° standard silver nitrate titrated with phosphate mixtures

Measured volumes of the standard silver nitrate solution, molarity = 0.04159, were introduced into a cell equipped with platinized conductance electrodes, diluted to 100 ml, permitted to come to temperature in a 12° water bath, and titrated with each phosphate mixture, stirring continuously. With each increment of added titrant a conductance value was recorded. These conductance values were corrected for the change in volume during the titration by multiplying each recorded figure by the original volume plus added increments divided by the original volume. The titration end-points were determined from a plot of conductance values against volume of phosphate mixture added. A sharp change in the slope of the curve marked the actual end-point. Silver nitrate solution was standardized[8].

The determination of total phosphate by the magnesia method

Measured aliquots from synthetic mixtures containing 0.2 – 0.35 g solids were diluted to 100 ml; 10 ml concentrated hydrochloric acid and 2 ml concentrated nitric acid were added. The mixture was boiled gently for 45 min. These samples were then chilled and analyzed for total phosphate by precipitation of magnesium ammonium phosphate, followed by ignition to magnesium pyrophosphate[5,6].

CONCLUSIONS

Comparative phosphate analyses by the new method and the BELL procedure has revealed the former to be more accurate in the majority of cases. However, the new analysis is limited to aqueous mixtures of linear phosphates containing no foreign ions which would interfere with the conductance titration using silver nitrate. For this reason it is suggested that the BELL procedure has wider analytical application.

SUMMARY

A new method for analysis of sodium ortho-, pyro-, and triphosphate is reported. This procedure consists of the measurement of three values which permit a simultaneous solution of three independent equations, yielding the relative amounts of linear phosphates present in the mixture. The measured quantities were: 1) pyrophosphate, gravimetrically determined as zinc pyrophosphate, reprecipitated at 19° and at a pH of 4.0 – 4.5, 2) silver phosphate, determined by a conductance titration at 12°, of standardized silver nitrate solution, and 3) total phosphate, determined after complete hydrolysis to orthophosphate in hot acid solution.

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Received November 25th, 1957

A NEW METHOD — BASED ON PAPER CHROMOTOGRAPHY — FOR THE ESTIMATION OF THORIUM AND URANIUM IN MONAZITE

by

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Standard methods for the gravimetric estimation of thorium in monazite and for the gravimetric and volumetric estimation of uranium in minerals have been described[1]. The present work describes a new technique in which thorium and uranium are separated chromatographically from all the other elements present in monazite. Thorium is then estimated by EDTA titration, while uranium is estimated spectrophotometrically.

EXPERIMENTAL

Opening up of the ore[2]

Monazite sand (10 g) is powdered to about 100-mesh and added a little at a time to 25 ml conc. sulphuric acid in an evaporating basin, and the mixture is heated to about 200°C on a sand bath. Heating is continued (for about half an hour) with constant stirring until the batch has the consistency of stiff mud (i.e. it can just be stirred) and retains a deep grey colour. The paste is then transferred gradually, with stirring, into 100 ml distilled water, the temperature being kept below 25°C by continuous cooling in ice. The residue is filtered with suction, dried, and again extracted with a further 10 ml conc. sulphuric acid, and the extract then poured into 50 ml distilled water. The two filtrates are combined and the residue of silica discarded. The solution contains the rare earth elements, thorium and uranium, together with excess of sulphuric and phosphoric acids, and other impurities.

Conversion to oxides[2]

This solution is made alkaline by adding solid sodium hydroxide in small portions with constant stirring. The solution eventually becomes very hot and begins to boil, a white precipitate being continuously formed. The solution should not be made strongly alkaline. The hydrated oxides are washed several times by decantation with distilled water, the supernatant liquid being filtered into a sintered glass funnel (Pyrex No. 4) under suction. This washing by decantation is continued till the supernatant liquid becomes faintly alkaline. The hydrated oxides are then transferred quantitatively to the sintered glass funnel, and washed several times with small amounts of distilled water.

Conversion to nitrates[2]

The hydrated oxides are dissolved from the sintered glass funnel by warm 50% nitric acid into a clean, dry suction flask. First 30 ml of the warm acid are added and the contents stirred gently till no lumps are observed; the filter is then drained. Another 10 ml of warm acid are added to dissolve any remaining precipitate. The filter is again drained and then washed with five 5-ml portions of the warm nitric acid. The filtrate is allowed to cool, transferred quantitatively to a 100-ml volumetric flask and diluted to the mark with 50% nitric acid.

Separation of thorium – uranium zone

The apparatus is similar to that already in general use for paper chromatography[3] and consists of a glass trough supported in a glass tank (50 × 25 × 15 cm) tightly covered with a glass plate. In the trough is placed the freshly prepared solvent mixture which consists of 100 ml dioxan, 1 ml conc. nitric acid, 1 g antipyrine (phenazone) and 2.5 ml distilled water. A little of the solvent mixture is also placed at the bottom of the tank to keep the inside atmosphere saturated. The tank is kept at constant room temperature.

Filter paper sheets are cut into strips 18 cm × 52 cm and the trough height is adjusted to permit two of these strips to be hung, one on each side of the trough, with their top edges dipping into the solvent. Each of the two strips is pencilled as shown in Fig. 1. Drops (exactly 0.01 ml) of the monazite sand solution are placed individually on the starting line of every second pencilled strip (on the small crosses) leaving the first as a blank. The drops are allowed to dry; then the top edges of the papers are placed in the trough and the tank is closed. The filter paper sheets are allowed to stand in the tank until the solvent front is about 5 cm from the lower edge of the paper. This usually takes about 10 h. It is essential that the solvent front of each chromatogram be strictly horizontal. The two chromatograms are removed from the tank and dried in a stream of hot air.

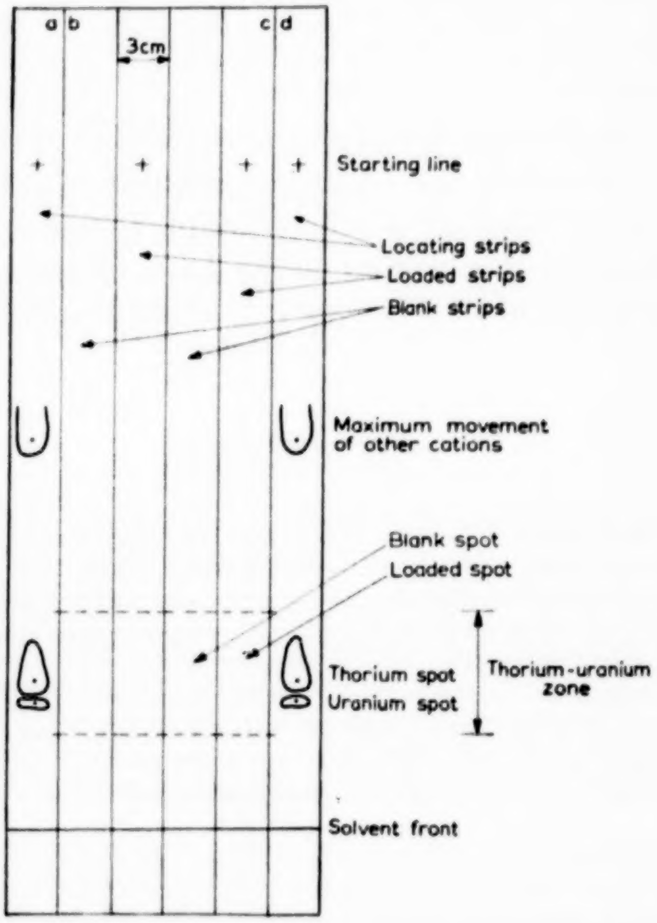

Fig. 1. Spot chromatogram for thorium estimation.

The two locating strips are cut out from each sheet, sprayed with kojic acid–oxine spray[4], allowed to dry and then viewed under ultra-violet light while held over concentrated aqueous ammonia in a 250-ml beaker. The thorium appears as a yellowish-green faintly fluorescent spot, while uranium appears as a black spot. The presence of thorium and uranium can be confirmed on fresh locating strips by the use of diphenylcarbazone and potassium ferrocyanide sprays, respectively[4]. The thorium spot moves with an R_F value of 0.78, while the uranium spot moves with an R_F value of 0.81, *i.e.* spots of thorium and uranium move almost together. On the other hand the maximum R_F values for the other elements in this solvent never exceed 0.41, thus leaving an appreciable space between the thorium–uranium zone and the other elements. This is best shown by the kojic acid–oxine spray. The thorium and uranium spots must be taken together since it is not possible — with this solvent mixture — to separate them on the paper strip. The position of thorium–uranium zone is marked with a pencil. The locating strips of each sheet are placed back in position beside the main chromatogram. The positions of the thorium–uranium zones are marked, with a pencil, on the main chromatograms. Then from the main chromatograms, loaded and blank thorium–uranium spots are cut out and collected in two glass containers.

Estimation of thorium[5]

One blank spot is cut into narrow snippets and placed in a 100-ml conical flask. 25 ml of distilled water are added, then 5 drops of 0.1 N nitric acid and 4 ml of exactly 0.001 M EDTA solution. The contents are boiled gently for about 5 min on a low-temperature hot plate. The flask is allowed to cool to room temperature and then precisely 5 or 6 ml 0.001 M bismuth nitrate solution are added, followed by 2–3 drops of 0.1% pyrocatechol violet indicator solution. If the solution is of the correct acidity it will immediately acquire a blue tint; if the colour is violet, the acidity is too great and it must be adjusted to pH 2–3 by cautious addition of aqueous ammonia solution and using universal indicator paper. The correct pH will be indicated by the appearance of the blue tint. The solution is then titrated with 0.001 M EDTA solution (from a micro-burette) very slowly until the colour changes to clear yellow. The total consumption of EDTA solution less the consumption of bismuth nitrate solution gives the value for the blank spot. The extraction and titration are repeated with another three blank spots and the mean value calculated.

One loaded spot is cut, extracted, and titrated as indicated above. The EDTA value for the loaded spot is calculated similarly. The process is repeated with another three loaded spots and the mean value calculated. By subtracting the mean value of the blank, the result is the mean value for thorium. The presence of uranium on the loaded spots does not interfere with the estimation of thorium by EDTA titration[5].

This procedure of separation and estimation proved to be extremely accurate when pure thorium nitrate solutions were used. The results are given in Table I.

TABLE I

Expt. No.	*μg of thorium*		*Error*
	present	*found*	
1	85	84.8	0.2
2	60	60.8	0.8
3	45	44.5	0.5
4	35	35.7	0.7
5	20	20.9	0.9

Separation of uranium–thorium zone

Filter paper sheets are cut as before, and each paper strip is pencilled as shown in Fig. 2. Ten loaded, as well as, ten blank strips should be prepared for each determination.

Drops (exactly 0.01 ml) of the monazite sand solution are placed along the starting line of the middle area — of each loaded strip — as well as on the locating strips of loaded and blank strips (*i.e.* on the small crosses). The drops are allowed to dry, and the separation is carried out as for the thorium–uranium zone. Uranium (on the loaded strips) is located by spraying the locating strips with the potassium ferrocyanide spray[4]. The zone carrying uranium (and some thorium) is cut out from each strip. Ten zones should be collected carrying the uranium in 100 drops of the monazite sand solution. Ten blank zones are similarly located and cut out from the blank strips.

The extraction should be carried out in a large Soxhlet extractor provided with a 500-ml flask. The ten zones — blank or loaded — are each folded several times along the long axis in a zigzag form and then introduced together into the extractor tube and should stand vertically. In the extractor flask about 150 ml of ethanol are placed. The paper zones in the extractor tube are then covered with sufficient ethanol and two ml of concentrated nitric acid are added (to ensure the presence of uranium on zones in the form of uranyl nitrate). The zones are allowed to soak for at least 2 h or preferably overnight. Extraction is then started and should be continued for at least 10 h. At the end of this period the condenser and extractor tube are removed, and the extract is evaporated to a volume of 150 ml while still in the flask. The extract is cooled to room temperature, and 150 ml of 3% aqueous solution of sodium carbonate are added in small amounts to remove acidity. It is then evaporated till the volume is about 50 ml by which time almost all the alcohol will be removed, cooled to room temperature, and kept till all the other duplicate samples of loaded and blank extracts are ready. Then all prepared samples are treated at the same time according to the following procedure. Two grams of powdered sodium carbonate are added to each extract and allowed to dissolve at room temperature. Then 10 ml of 3% hydrogen

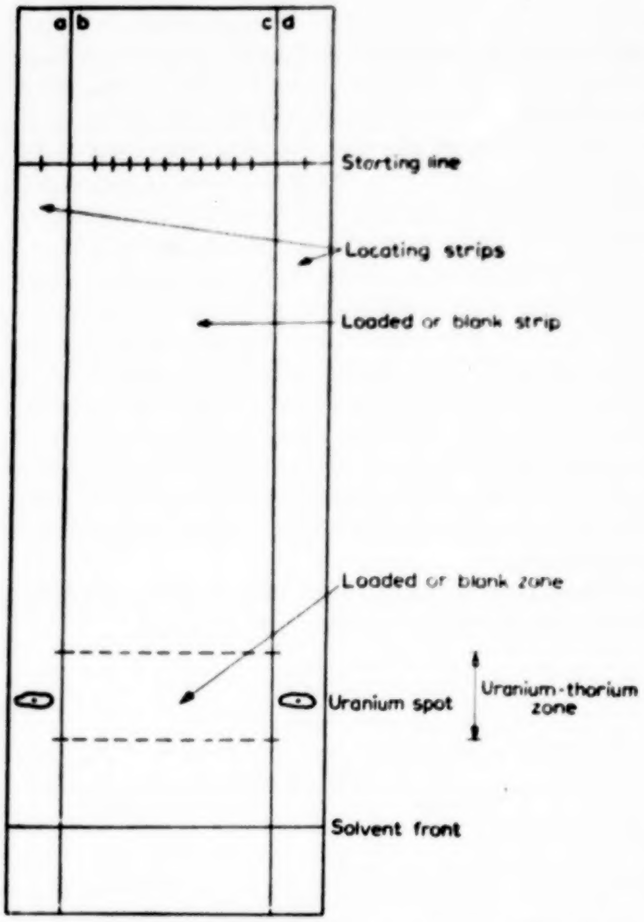
a
b
c
d
Starting line
Locating strips
Loaded or blank strip
Loaded or blank zone
Uranium spot
Uranium-thorium zone
Solvent front

Fig. 2. Zone chromatogram for uranium estimation.

peroxide solution are added. The loaded extracts acquire a pale yellow colour, and at the same time a gelatinous white precipitate appears. The yellow colour is due to the formation of uranium peroxide ($UO_4.H_2O$)[6], which dissolves in sodium carbonate solution. The gelatinous precipitate is hydrated thorium peroxide[6], which is practically insoluble in sodium carbonate solution. Blank and loaded extracts are filtered through sintered glass crucibles (Pyrex No. 4), under suction. Any precipitate remaining is washed several times with small amounts of 10% sodium carbonate solution. The filtrates are transferred quantitatively to 100-ml measuring flasks and diluted to the mark

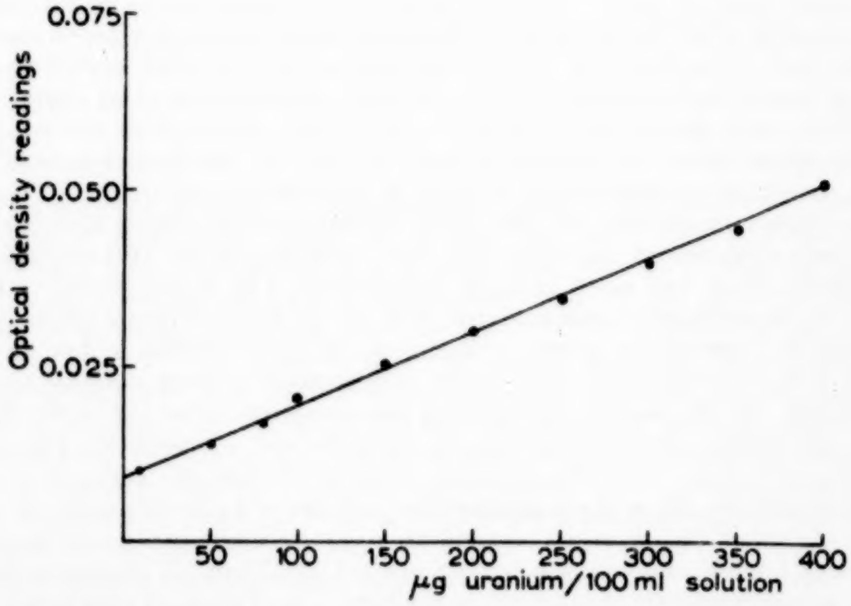

Fig. 3. Calibration graph for the spectrophotometric determination of uranium.

with distilled water. Two types of filtrate must be available, the blank filtrate from the extraction of blank zones and the uranium filtrate of the loaded zones. The two filtrates are now ready for the spectrophotometric estimation, which should be carried out immediately since the yellow colour of the solution is unstable and fades slowly within 2 or 3 h.

Estimation of uranium[7]

The estimation of uranium is carried out spectrophotometrically by the use of hydrogen peroxide solution in sodium carbonate medium. Standard solutions of uranium are prepared to contain from 10–400 μg uranium per 100 ml solution. To each solution is added 25 ml 10% sodium carbonate solution and 10 ml 3% hydrogen peroxide solution, and the mixture is diluted to the mark with distilled water. A blank solution is also prepared. A calibration curve is drawn for the available spectrophotometer, using the prepared blank and uranium standard solutions. The curve appears as shown in Fig. 3 using a wavelength of 400 mμ and 5-cm cells.

This procedure of separation, extraction, and estimation, proved to be fairly accurate when carried out starting with standard pure uranyl nitrate solutions. The results are given in the Table II.

TABLE II

Expt. No.	*μg percent of uranium*		*Error*
	present	*found*	
1	117	114	3
2	222	224	2
3	76	78	2
4	330	332	2
5	375	378	3

RESULTS

For application of the technique described above, a sample of Egyptian monazite was used. The Egyptian monazite forms the nonmagnetic portion of the black sand obtained from the Mediterranean coast between the city of Rosetta and Borollos Lake. The mineral sample was obtained in the form of a brownish-coloured sand finely powdered to about 100 mesh.

Estimation of thorium

Five experiments on monazite sand solutions gave a value of 4.267 ± 0.002 g thorium per 100 g sand (each reading is the mean of six EDTA titrations). The value for thorium obtained by standard methods was 4.260 g %.

Estimation of uranium

The apparatus used was the Carl Ziess spectrophotometer model PMQ II, using a wavelength of 400 mμ, an additional colour filter of 380–500 mμ and 5-cm glass cells.

For the estimation, five uranium and five blank extracts were prepared from five monazite sand solutions. The values obtained were 0.051 ± 0.002 g uranium per 100 g sand. The value for uranium obtained by standard methods was 0.050 g %.

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DISCUSSION

The technique described above depends on the separation of thorium and uranium from the other cations present in the monazite sand solution. The determination of thorium proved to be successful in the presence of uranium by indirect titration with standard $0.001 M$ EDTA solution[5] and the presence of thorium in the uranium extract did not interfere with the determination of uranium. This new method proved to be fairly accurate. However, there are certain points to consider in order to obtain the best results.

1. The dioxan solvent mixture used for the separation must be freshly prepared. The freshly prepared solvent mixture is almost colourless; after 48 h, it acquires a pale yellow colour which will stain the paper strips and will seriously interfere with the determination of uranium.
2. It was mentioned that the R_F values for thorium and uranium are 0.78 and 0.81, respectively. In a previous paper[4] the R_F values for thorium and uranium were given as 0.64 and 0.70 respectively. The increase in the R_F values in the second case is due to the presence of 50% nitric acid in the monazite sand solution, while in the first case thorium and uranium salts were dissolved in $0.1 N$ nitric acid.
3. The estimation of thorium was carried out by an indirect method; 4 ml of EDTA were added, and boiling was effected to extract the cations contained on the paper. Back titration with $0.001 M$ bismuth nitrate solution proved unsatisfactory. Then 5 or 6 ml bismuth nitrate solution were accurately added to furnish sufficient bismuth ions in solution to bring the colour of indicator to blue at a pH of 2 or 3[5]; if only 4 ml bismuth nitrate solution are added, the colour of the indicator at this pH value is pink.
4. It is important in this type of analysis to use A.R. reagents as well as filter paper sheets specified for chromatography.

SUMMARY

A dioxan-antipyrine solvent mixture is used to separate thorium and uranium — on sheet chromatograms — from the monazite sand solution. Thorium is estimated by an indirect EDTA titration method, using pyrocatechol violet. Uranium is estimated spectrophotometrically by the hydrogen peroxide method.

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Received December 12th, 1957

PAPER CHROMATOGRAPHY IN THE SEPARATION OF IONS

II. SEPARATION OF PRECIOUS METALS

by

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An attempt to separate quite a large number of ions by ascending paper chromatography with a solvent mixture containing water, acetone and hydrochloric acid, resulted in an excellent separation of at least seven common ions from a mixture[1]. LEDERER[2] in his series of publications showed the effectiveness of the solvent butyl alcohol for the separation of the platinum metals, present in a ternary or a quaternary mixture. Methyl ethyl or methyl *n*-propyl ketone admixed with hydrochloric acid was utilized by BURSTALL *et al.*[3] in their separation of Rh, Pd, Pt and Au. KEMBER AND WELLS[4] recommended the use of solvents such as (i) hexone, pentanol and hydrochloric acid, (ii) *n*-butanol saturated with 3N hydrochloric acid and (iii) solvent (ii) containing hydrogen peroxide for the separation of Pd, Pt, Rh and Ir.

The separation of the precious metals, Pd^{+2}, Pt^{+4}, Ir^{+4}, Rh^{+3}, Ru^{+3}, Os^{+4} and Au^{+3}, in the presence of a masking agent, such as thiourea, is feasible even if there are five such ions present in a mixture. Using other complexing agents such as ammonium iodide, bismuthiol I, bismuthiol II and 2-mercaptobenzothiazole separation of a ternary or a quaternary mixture can be achieved. Some of the solvents employed failed to give satisfactory separation of ions, which was also observed with circular paper chromatography[5]. The latter method, though preferred for its simplicity and speed, gives overlapping zones with ions; whose R_F values are closer than are usually separated with the ascending technique.

EXPERIMENTAL

The apparatus used, the procedure followed and the solutions of the precious metals were the same as those described in previous papers[1,5].

The following developing solvents (A to R) were prepared from acetone or *tert.*-butyl alcohol, water, and hydrochloric acid (sp.gr. 1.19) or acetic acid (sp.gr. 1.055) in varying ratios; some contained ammonium iodide, thiourea, bismuthiol I, bismuthiol II or 2-mercapto-benzothiazole to form undissociated complexes.

A Acetone, water and hydrochloric acid in the ratio 70:20:10
B Acetone, water and acetic acid, 70:20:10
C Acetone, water and acetic acid, 70:25:5
D Solvent B with 2 g ammonium iodide
E Solvent C with 2 g ammonium iodide
F *tert.*-Butyl alcohol, water and hydrochloric acid, 70:20:10
G *tert.*-Butyl alcohol, water and acetic acid, 70:20:10
H Solvent G with 2 g ammonium iodide
I Solvent A with 2 g thiourea
J Solvent B with 2 g thiourea
K Solvent F with 2 g thiourea
L Solvent G with 2 g thiourea
M Solvent B with 2 g bismuthiol II

TABLE I

R_L AND R_T VALUES AT 30–35°

Solvent	Pd^{+2}		Pt^{+4}		Ir^{+4}		Rh^{+3}		Ru^{+3}		Os^{+4}		Au^{+3}	
	RL	RT	RL	RT	RL	RT	RL	RT	RL	RT	RL	RT	RL	RT
A	1.00	0.94	1.00	0.98	0.26	0.18	0.49	0.34	0.18	0.13	0.98	0.96	1.00	0.98
B	0.97	0.51^{dc}	0.80	0.76^{ds}	0.20	0.17	0.18	0.07	0.28	0.19	0.64	0.61	1.00	0.97
			0.52	0.46										
C	1.00	0.48^{dc}	0.88	0.84^{ds}	0.32	0.22	0.36	0.23	0.31	0.23	0.80	0.75	1.00	0.96
			0.69	0.64										
D	0.98	0.90	0.97	0.86	0.41	0.31	1.00	0.00^{dc}	0.28	0.18	0.63	0.59	0.75	0.69
E	1.00	0.94	1.00	0.95	0.43	0.37	1.00	0.00^{dc}	0.34	0.25	0.74	0.70	0.85	0.79
F	0.90	0.83	0.90	0.84	0.25	0.18	0.33	0.25	0.10	0.04	0.92	0.87	1.00	0.97
G	0.73	0.09^{dc}	0.33	0.00^{dc}	0.27	0.13	0.13	0.03	0.19	0.10	0.41	0.02^{dc}	0.85	0.35^{dc}
H	0.43	0.38	0.51	0.30^{dc}	0.30	0.23	0.08	0.00	0.10	0.00	0.11	0.06	0.63	0.52
I	0.93	0.84	1.00	0.95	0.44	0.38	0.64	0.58	0.21	0.13	1.00	0.99	1.00	0.90
J	0.86	0.76	0.88	0.86^{dd}	0.38	0.33	0.56	0.48	0.12	0.03	0.74	0.70	0.86	0.81
			0.85	0.81										
K	1.00	0.91	0.95	0.80	0.33	0.21	0.22	0.13	0.09	0.02	0.93	0.82	0.95	0.78^{dc}
L	0.49	0.22^{dc}	0.70	0.18^{dc}	0.33	0.08^{dc}	0.16	0.00^{dc}	0.04	0.00	0.50	0.04^{dc}	0.91	0.84
M	1.00	0.96	0.78	0.71^{dd}	0.34	0.28	1.00	0.37^{dc}	0.07	0.05	0.82	0.77	0.98	0.95
			0.71	0.66										
N	0.62	0.10^{dc}	0.53	0.03^{dc}	0.06	0.00	0.43	0.00^{dc}	0.06	0.00	0.62	0.01^{dc}	0.61	0.36^{dc}
O	0.18	0.10	0.67	0.45^{dc}	0.13	0.04	1.00	0.01^{dc}	0.06	0.00	0.71	0.67	0.68	0.55
P	0.29	0.07^{dc}	0.44	0.26^{dc}	0.30	0.16	0.14	0.00^{dc}	0.03	0.00	0.34	0.02^{dc}	0.43	0.30
Q	0.11	0.00	0.63	0.58^{dd}	0.06	0.01	0.79	0.06^{dc}	0.13	0.05	0.72	0.68	0.80	0.70
			0.52	0.00										
R	0.28	0.00^{dc}	0.70	0.00^{dc}	0.42	0.18^{dc}	0.62	0.00^{dc}	0.28	0.19	0.73	0.04^{dc}	0.86	0.65^{dc}

^{dc} = diffuse comet-like; ^{dd} = diffuse discontinuous; ^{ds} = sharp discontinuous.

N Solvent G with 2 g bismuthiol II
O Solvent B with 2 g bismuthiol I
P Solvent G with 2 g bismuthiol I
Q Solvent B with 2 g 2-mercaptobenzothiazole
R Solvent G with 2 g 2-mercaptobenzothiazole.

TABLE II

Solvent	*Sequences of separation*
A	Pd–Rh–Ir–Ru, Pt–Rh–Ir–Ru, Au–Rh–Ir–Ru, Os–Rh–Ir–Ru
B or C	Au–Os–Pt–Ir, Au–Os–Pt–Rh, Au–Os–Pt–Ru
D or E	Pd–Au–Os–Ir, Pt–Au–Os–Ir, Pd–Au–Os–Ru, Pt–Au–Os–Ru
F	Au–Pd–Rh–Ru, Au–Os–Rh–Ru, Au–Pt–Rh–Ru, Au–Pd–Ir–Ru, Au–Os–Ir–Ru, Au–Pt–Ir–Ru
H	Au–Pd–Ir–Rh, Au–Pd–Ir–Os, Au–Pd–Ir–Ru
I	Os–Pd–Rh–Ir–Ru, Au–Rh–Ir–Ru, Pt–Rh–Ir–Ru
J	Au–Os–Rh–Ir–Ru
L	Au–Pd–Rh, Au–Pd–Ru
M	Au–Os–Ir–Ru, Pd–Os–Ir–Ru, Au–Pt–Ir–Ru, Pd–Pt–Ir–Ru
O	Au–Pd–Ru, Os–Pd–Ru, Pt–Pd–Ru

To show whether a separation is possible, R_L and R_T values and not R_F values are recorded in Table I. In Table II the sequences of separation are presented. Separations were not possible with solvents G, K, N, P, Q and R. Solvents A, B, D, F and H gave the same order of separations as found with circular paper chromatography[5]. As complexing agents, ammonium iodide, bismuthiol I, bismuthiol II and 2-mercaptobenzothiazole were chosen because of their solubility in acetone and *tert.*-butyl alcohol and their great tendency to form complexes with the precious metals.

Platinum often gave more than one band, either short and sharp or long and diffuse. Short bands observed with Pt might be due to complexes at different valence states. Long and discontinuous bands, usually associated with Pt in the presence of thiourea, bismuthiol II and 2-mercaptobenzothiazole, could be explained as spreading due to the slight solubility of the complexes in the solvents. Higher solubility of the metals in hydrochloric acid gave rise to narrower bands, as compared with acetic acid. The mobilities of the Ir and Ru ions were affected least by the complexing agents used. With thiourea, the mobilities of Pd and Au were less than that of Rh. Ammonium iodide, thiourea, bismuthiols and 2-mercaptobenzothiazole not only restricted or modified the movement of the ions, but also served as chromogenic agents for Pd, Pt, Rh and Os.

SUMMARY

A study of the separation of the precious metals, Pd^{+2}, Pt^{+4}, Ir^{+4}, Rh^{+3}, Ru^{+3}, Os^{+4} and Au^{+3}, by ascending paper chromatography, using different solvents and a number of complexing agents, clearly shows that microgram amounts of the elements, when present in a mixture of five, are best separated from each other in the presence of thiourea. The R_L, R_T values and the sequences of separation are recorded in tables to show whether a good separation of a particular mixture of ions is possible.

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Received November 11th, 1957

PAPER CHROMATOGRAPHY IN THE SEPARATION OF IONS

III. SEPARATION OF SILVER, COPPER AND ARSENIC GROUP ELEMENTS

by

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This paper records the results of a series of attempts, to separate elements belonging to the silver, copper and arsenic groups on paper strips with a number of solvents[1] prepared from acetone or *tert.*-butyl alcohol, water, and acetic or hydrochloric acid. Complexing agents such as ammonium iodide, thiourea, bismuthiol I, bismuthiol II and 2-mercaptobenzothiazole were sometimes added separately to the solvents to study their effect on the movement of the ions.

The formation of a soluble complex is indicated by a more rapid movement, higher R_F value and the formation of distinct spots with less diffusion, whereas the formation of insoluble compounds is shown by lower R_F values. Owing to the continued action of the solvent on a precipitated complex, this partly dissolves and a comet-shaped continuous band or distinct disconnected bands appear (*cf.* Table I). The presence of 1–2% of the complexing agent is sufficient to promote the formation of stable complexes, with different solubilities and distribution coefficients.

The R_F values are also influenced by the nature of the organic solvents, for instance, in acetone the movements of the ions are faster, whilst in *tert.*-butyl alcohol, the movements are rather slow. Of the ions tested, silver shows no movement and, even with the complexing agents, its rate is slow. In the presence of hydrochloric acid the ions move faster owing to the higher solubility, and the spot area is smaller. Lead, silver, bismuth and antimony are precipitated in the presence of acetic acid and give long, diffused bands which are more pronounced with the complexing agents. The rate of movement of the bismuth–bismuthiol II complex is very high compared to the complexes of bismuth with 2-mercaptobenzothiazole and bismuthiol I; the latter moves slowest. Thallium forms a soluble complex with 2-mercaptobenzothiazole and moves considerably, while with the bismuthiols it precipitates. Arsenic is considered to be inactive towards complexing substances for it maintains the same movement all through the tests.

The R_L, R_T values and the sequences of separation are recorded in Tables I and II respectively. In Table II, the ions enclosed in brackets have a portion of their migration zone in common. No satisfactory separation of ions is possible with the solvents J, L, N and P, because of the spreading and the overlapping of the zones.

EXPERIMENTAL

The apparatus, solvents (A to R) and solutions used and the procedure adopted were the same as those described in earlier papers[1,2].

TABLE I

R_L AND R_T VALUES AT 30–35°

Solvent	Hg^{+2}		Ag^{+}		Pb^{+2}		Tl^{+}		Cu^{+2}		Cd^{+2}		Bi^{+3}		As^{+3}		Sb^{+3}	
	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T	R_L	R_T
A	1.00	0.97	0.93	0.89	0.72	0.68	0.04	0.00	0.82	0.77	1.00	0.96	1.00	0.96	0.80	0.75	1.00	0.96
B	0.98	0.94	0.25	0.00^{dc}	0.20	0.15	0.19	0.05	0.34	0.27	0.62	0.58	0.53	0.48	0.48	0.40	0.79	0.12^{dc}
C	0.98	0.94	0.26	0.00^{dc}	0.20	0.15	0.21	0.09	0.36	0.28	0.63	0.58	0.41	0.02^{dc}	0.48	0.40	0.29	0.12
D	0.98	0.96	0.66	0.63	0.65	0.62	0.05	0.01	0.87	0.79	0.75	0.73	0.72	0.67	0.45	0.38	0.32	0.26
E	0.98	0.96	0.75	0.72	0.78	0.73	0.07	0.01	0.90	0.83	0.75	0.72	0.78	0.73	0.50	0.45	0.27	0.21
F	1.00	0.95	0.00	0.00	0.20	0.10	0.04	0.00	0.32	0.26	1.00	0.95	0.83	0.75	0.55	0.47	1.00	0.92
G	0.71	0.60	0.36	0.00^{dc}	0.21	0.15	0.19	0.14	0.28	0.14	0.36	0.27	0.37	0.00^{dc}	0.40	0.29	0.40	0.00^{dc}
H	0.75	0.69	0.26	0.18	0.10	0.00	0.11	0.04	0.35	0.29	0.53	0.48	0.63	0.58	0.44	0.40	0.43	0.00^{dc}
I	1.00	0.96	0.90	0.70^{dc}	0.74	0.04^{dc}	0.03	0.00	1.00	0.91	1.00	0.96	1.00	0.98	0.74	0.68	1.00	0.97
J	1.00	0.70^{dd}	0.74	0.66	0.54	0.32^{dc}	0.38	0.10^{dc}	0.79	0.72	0.76	0.64	0.73	0.47^{dd}	0.47	0.41	0.47	0.08^{dc}
	0.56	0.49											0.28	0.19^{dd}				
K	1.00	0.60^{dc}	0.27	0.12	0.36	0.22	0.03	0.00	1.00	0.80^{dc}	0.97	0.90	0.84	0.76	0.63	0.55	1.00	0.93
L	0.62	0.47^{dd}	0.59	0.43	0.46	0.11^{dc}	0.12	0.02	0.51	0.43	0.62	0.50	0.55	0.41	0.50	0.47	0.23	0.00^{dc}
	0.10	0.00																
M	0.88	0.61^{dc}	0.06	0.02	0.21	0.02^{dc}	0.04	0.00	0.85	0.35^{dc}	0.60	0.50	1.00	0.97	0.45	0.40	0.34	0.20
N	0.61	0.36^{dd}	0.20	0.00^{dc}	0.22	0.00^{dc}	0.06	0.00	0.32	0.00^{dc}	0.48	0.25	0.63	0.01^{dc}	0.41	0.34	0.35	0.00^{dc}
	0.09	0.00																
O	1.00	0.04^{dc}	0.06	0.00	0.40	0.16^{dc}	0.30	0.01^{dc}	0.12	0.00	0.65	0.57	0.31	0.02^{dc}	0.46	0.42	0.26	0.03^{dc}
P	0.43	0.00^{dc}	0.16	0.00^{dc}	0.14	0.00^{dc}	0.01	0.00	0.17	0.00^{dc}	0.52	0.00^{dc}	0.09	0.00	0.38	0.29	0.35	0.00^{dc}
Q	0.64	0.00^{dc}	0.04	0.00	0.38	0.27	0.33	0.16	0.09	0.00	0.66	0.60	0.60	0.01^{dc}	0.42	0.37	0.31	0.03^{dc}
R	0.62	0.00^{dc}	0.11	0.00	0.33	0.24	0.28	0.22	0.10	0.00	0.52	0.39	0.53	0.00^{dc}	0.45	0.37	0.32	0.00^{dc}

^{dc} = diffuse comet like; ^{dd} = diffuse discontinuous.

TABLE II

Solvent	*Sequence of separation*
A	Hg–Ag–Cu–Pb–Tl, Cd–Cu–Pb–Tl, Bi–Cu–Pb–Tl
B	Hg–Cd–Bi–As–Cu, Hg–Cd–Bi–Cu–Pb, Hg–Cd–Bi–Cu–Tl, Hg–Cd–Bi–Ag
C	Hg–Cd–Cu–Tl, Hg–Cd–Cu–Pb, Hg–Cd–Cu–Sb, Hg–Cd–As–Sb
D	Hg–(Cu–Cd)–Ag–Tl, Hg–(Cu–Cd)–Pb–Tl, Hg–(Cu–Cd)–As–Sb, Hg–Cu–Bi–As–Sb, Hg–Cu–Bi–Tl
E	Hg–Cu–Cd–As–Sb, Hg–Cu–Bi–As–Sb, Hg–Cu–Cd–Tl, Hg–Cu–Ag–Tl, Hg–Cu–Bi–Tl, Hg–Cu–Pb–Tl
F	Hg–Bi–Cu–Pb–Tl, Hg–Bi–Cu–Pb–Ag, Cd–Bi–Cu–Pb–Tl, Cd–Bi–Cu–Pb–Ag, Hg–Bi–As–Cu, Cd–Bi–As–Cu, Sb–Bi–As–Cu
G	Hg–Cd–Pb, Hg–Cd–Tl
H	Hg–Bi–Cd–Ag–Tl, Hg–Bi–Cd–Ag–Pb, Hg–Bi–Cd–Cu, Hg–Bi–As–Cu
I	Hg–Ag–Tl, Bi–Ag–Tl, Cd–Ag–Tl
K	Cd–Bi–Ag–Tl, Hg–Ag–Tl, Cd–Bi–Pb, Sb–Bi–As, Cd–Bi–As
M	Bi–Hg–As–Sb, Bi–Cd–As–Sb, Bi–Hg–Tl, Bi–Hg–Pb, Bi–Hg–Ag, Bi–Cu–Tl, Bi–Cu–Pb, Bi–Cu–Ag, Bi–Cd–Tl, Bi–Cd–Pb, Bi–Cd–Ag
O	Cd–Pb–Ag, Cd–As–Cu, Cd–As–Sb, Cd–As–Bi
Q or R	Cd–Tl–Cu, Cd–Pb–Cu, Cd–Tl–Ag, Cd–Pb–Ag
Q	Cd–As–Sb.

SUMMARY

A paper chromatographic study of the separability of ions of elements of the silver, copper and arsenic groups, using different solvents and a number of complexing agents, reveals that the solvents consisting of (1) acetone, hydrochloric or acetic acid (with or without ammonium iodide) and (2) *tert.*-butyl alcohol, hydrochloric or acetic acid, promote the complete separation of at least five elements present in microgram amounts in a mixture. Other complexing agents, such as thiourea, bismuthiol I, bismuthiol II and 2-mercaptobenzothiazole are not very useful in the separation of the ions. The R_f, R_T values and the sequences of separation are tabulated to show their behaviour.

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Received November 11th, 1957

SOLUBILIZATION CHROMATOGRAPHY

II. KETONES

by

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Salting-out chromatography, a technique whereby nonelectrolytes are separated by elution with aqueous salt solutions through a column of ion-exchange resin, has been applied successfully in this laboratory to mixtures of lower alcohols[1], amines[2], ethers[3], and ketones[4]. The phenols and higher alcohols have been separated by chromatography through ion-exchange resins with aqueous solutions of acetic acid as eluents[5]. This method has been designated solubilization chromatography and is applied in the present paper to the study of ketones of higher molecular weight.

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The equation[6]

$$U^* = CV + V \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

is used to interpret the results of the study. (U^* is the volume of effluent collected from the addition of the sample to the peak of the elution graph, C is the distribution ratio of the ketone between the resin phase and the aqueous phase, and V is the interstitial volume of the resin bed).

EXPERIMENTAL

Ketones

The ketones used were of the best grade commercially available. No further purification was necessary.

Eluents

Solutions of eluents were prepared by dilution of reagent-grade glacial acetic acid, absolute ethanol, absolute methanol (free of aldehydes and ketones), and C.P. propanol-2.

The Eastman-grade tetraethylammonium bromide used to prepare eluent solutions was found to contain a strong acid, and such eluents were neutralized to a pH of 7 with tetraethylammonium hydroxide before use.

Resins

The strong-acid cation-exchange resin, Dowex-50, in the hydrogen and tetraethylammonium forms, and the strong-base anion-exchange resin, Dowex-1, in the bromide form, were used exclusively to study the higher ketones. These resins had proved most satisfactory in the solubilization chromatography of the phenols and alcohols[5]. In each case the resins were of 200–400 mesh and crosslinked with 8% divinyl benzene.

The hydrogen form of Dowex-50 was converted to the tetraethylammonium form by passing a 10% solution of tetraethylammonium hydroxide in water through the column until the pH of the effluent equalled the pH of the influent. This neutralization reaction may also be followed visually because the resin becomes a lighter brown color as it is converted to the tetraethylammonium form. The chloride form of Dowex-1 was converted to the bromide form by passing a large excess of saturated potassium bromide through the column. The absence of chloride in the effluent was confirmed by testing with silver nitrate and Miller's reagent[7].

The ratio of void volume to bed volume, V/V_B, was determined[3] and found to be 0.363 for Dowex-50-X8, lot No. 4226-28, and 0.423 for Dowex-1-X8, lot No. 4101-27.

Elutions

The samples were put onto the resin bed as previously described[1]. In general, 0.2 mmole of samples, dissolved in 1.0 ml of at least 50% of the particular eluent being used, was eluted with a flow rate of approximately 0.4 cm/min. Fractions of approximately 5.0 ml were collected automatically with a constant-volume collecting device[6].

Analysis

The concentration of ketone in the effluent was determined by two methods:

1. Fractions containing acetic acid were analyzed by mixing them with 5.0 ml of 0.1 N sodium dichromate in concentrated sulfuric acid, diluting with 25 ml of distilled water, and measuring the absorbance of the resulting Cr (III)[8].
2. Fractions containing alcohol or salt were analyzed by a modification of the differential pH method of ROE and MITCHELL[9,4]. 5 ml of 0.1 M hydroxylamine hydrochloride was added to each fraction with stirring, and the pH was determined after 5 min. The difference between this pH and that of an effluent fraction known to contain no ketone is proportional to the amount of ketone present.

Solubility studies

The relative solubilities of methyl *iso*propyl ketone and methyl *n*-propyl ketone in aqueous tetraethylammonium bromide solutions were determined by shaking an excess of each ketone with 0.00, 0.875, 1.25, 1.75, 2.50, and 3.50 M solutions of the salt. After allowing the phases to separate, the relative quantity of ketone in an aliquot of each aqueous phase was determined by the Δ pH method[9,4].

RESULTS AND DISCUSSION

Variables

Because the effects of such elution variables as mesh size and cross-linkage of resin, flow rate, and sample size have been well established for salting-out chromatography[1-4], and because these variables have been shown to effect solubilization chromatography in a similar manner[5], no such study was carried out with the higher ketones.

Because of the limited solubility of the higher ketones, it is generally not possible to dissolve the feed sample in 1 ml of the eluent solution. For this reason, more concentrated solutions of the organic constituent of the eluent were used as solvents for the samples. It was assumed that these variations in sample preparation would have no effect on the elution behavior of the ketones, as was shown to be the case with the phenols and higher alcohols[5].

Eluent study

In the solubilization chromatography of the higher alcohols, acetic acid was the only possible eluent because the spectrophotometric determination of the chromic ion produced by the reduction of dichromate[8] is the only convenient method for the determination of small concentrations of such compounds in effluent fractions, and

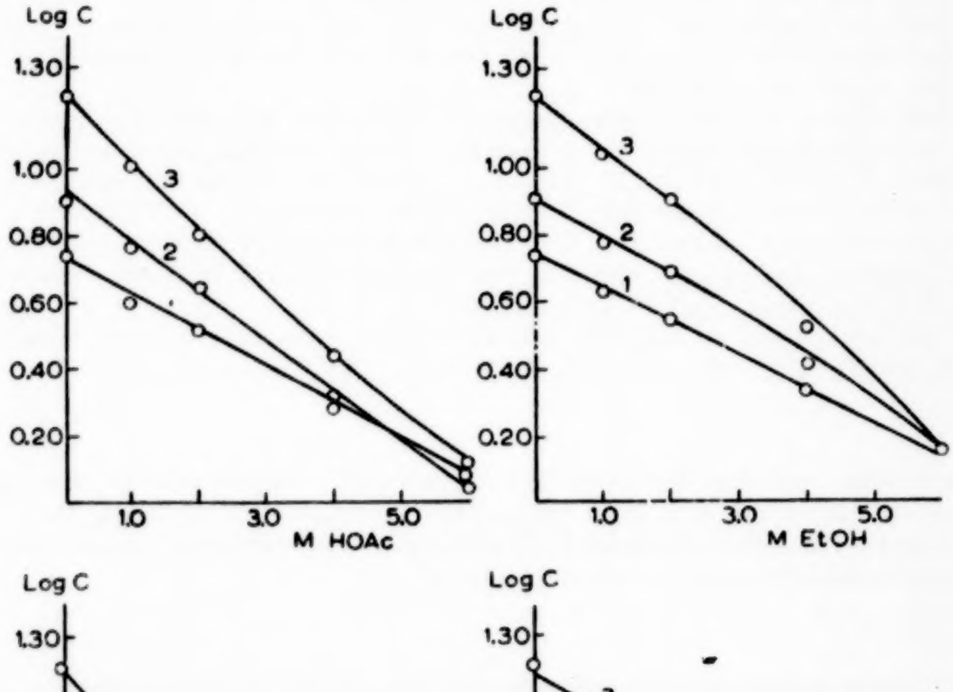

Fig. 1. Plots of Log *C* *vs.* *M* for three ketones with the eluents indicated. Dowex-50-X8, 200–400 mesh, hydrogen form. 1. methyl *n*-butyl ketone. 2. methyl *n*-amyl ketone. 3. methyl *n*-hexyl ketone.

acetic acid is one of the few organic compounds not oxidized by dichromate. However, the two methods of analysis available for ketone fractions suggested the study of a number of solubilizing agents with these compounds.

Methyl *n*-butyl, methyl *n*-amyl, and methyl *n*-hexyl ketones were eluted with various molarities of the solubilizing agents studied: methanol, ethanol, acetic acid, and propanol-2. Fig. 1 shows the results of plotting the logarithm of the distribution ratio, *C*, as calculated by equation (1), for these three ketones on Dowex-50-X8, hydrogen form, *vs.* the molarity of the different solubilizing agents. Tables I and II list, respectively, the *C* values for the different eluents, and the summary of the plots shown in Fig. 1. These data indicate the following:

1. None of the eluents used give completely linear plots of log *C* *vs.* *M* for all ketones studied (see also Table III). Many are linear for only a small region and tend to curve downward and converge at large molarities of the eluent. These same results were obtained for acetic acid elutions of the phenols and higher alcohols[5].

2. The slopes obtained from the linear portions of the plots for a given ketone are not constant with different eluents. It is seen that the order of effectiveness as solubilizing agents of the compounds studied, as measured by the magnitudes of the slopes in Table II, increases from methanol through propanol-2 as listed. This was to be expected because, as the organic nature of an eluent increases, its ability to dissolve a ketone from the resin increases.

3. A plot of log *C* *vs.* *M* for a given ketone begins to curve downward at lower molarities of eluent as the carbon content of that eluent increases. Thus it is seen that at 4*M* methanol, the plots for the three ketones studied are still straight lines and their *C* values are well separated, but the plots at 4*M* propanol-2 have severely converged and the *C* values are very similar. This is probably due to the fact that the three ketones have a greater differential solubility in 4*M* methanol than they do in 4*M* propanol-2.

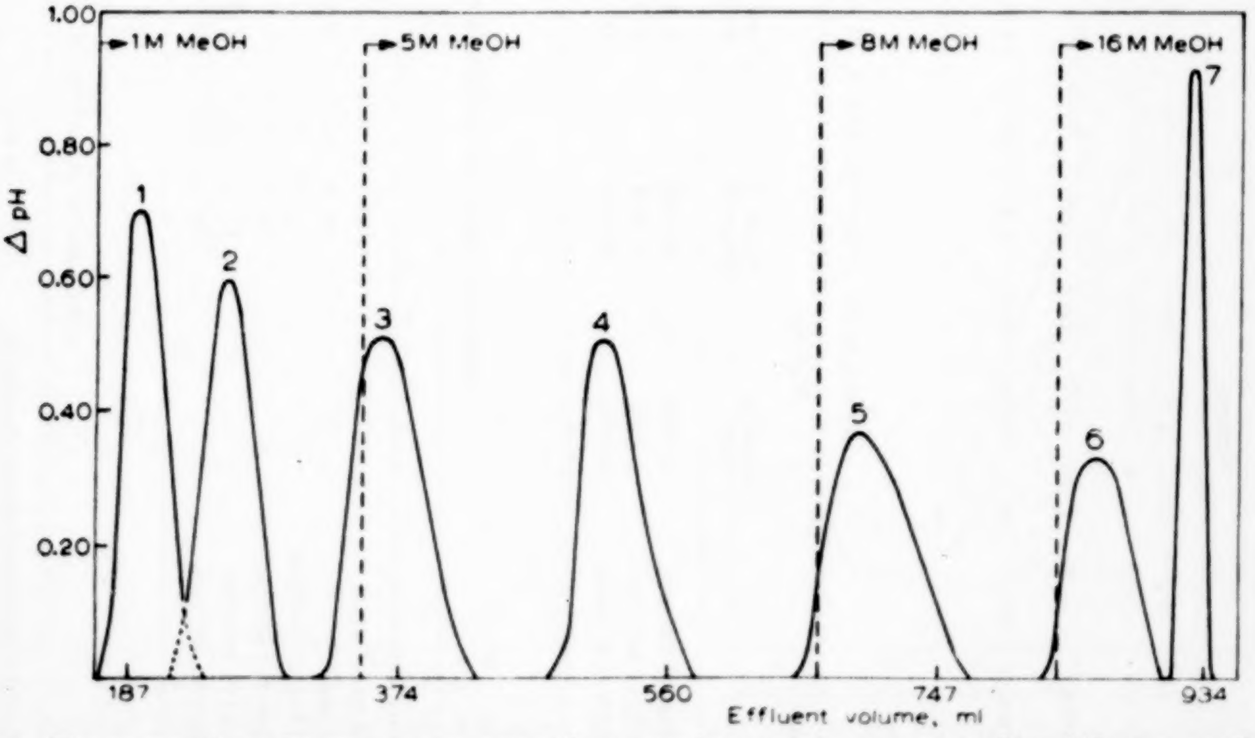

Fig. 2. The separation of a seven-component ketone mixture. 54.5 cm × 2.28 cm² Dowex-50-X8, 200–400 mesh, hydrogen form, 0.28 cm/min. Aqueous methanol eluent changed at 350 ml, 670 ml, and 835 ml. 1. methyl iso-butyl ketone. 2. methyl *n*-butyl ketone. 3. methyl *n*-amyl ketone 4. methyl *n*-hexyl ketone. 5. methyl *n*-heptyl ketone. 6. methyl *n*-octyl ketone. 7. methyl *n*-nonyl ketone.

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TABLE I

VALUES OF DISTRIBUTION RATIO, C, ON DOWEX-50-X8, HYDROGEN FORM, 200–400 MESH

Eluent	*Methanol*					*Ethanol*					*Acetic acid*					*Propanol-2*			
Molarity	0.0	2.0	4.0	6.0	8.0	0.0	1.0	2.0	4.0	6.0	0.0	1.0	2.0	4.0	6.0	0.0	1.0	2.0	4.0
Methyl *n*-butyl ketone	5.55	4.14	3.04	2.50	2.01	5.55	4.33	3.58	2.21	1.51	5.55	4.08	3.32	1.98	1.26	5.55	4.17	3.14	1.42
Methyl *n*-amyl ketone	8.26	5.95	4.00	3.23	2.40	8.26	6.13	4.96	2.66	1.47	8.26	6.00	4.41	2.10	1.12	8.26	5.03	3.84	1.47
Methyl *n*-hexyl ketone	16.4	10.1	6.94	4.93	3.30	16.4	11.3	8.16	3.36	1.45	16.4	10.4	6.46	2.77	1.33	16.4	9.17	6.00	1.60

TABLE II

RESULTS OF PLOTTING LOG C *vs.* M FOR DOWEX-50-X8, HYDROGEN FORM, 200–400 MESH

Eluent	*Methanol*		*Ethanol*		*Acetic acid*		*Propanol-2*	
	Negative slope	*Extent of linearity*	*Negative slope*	*Extent of linearity*	*Negative slope*	*Extent of linearity*	*Negative slope*	*Extent of linearity*
Methyl *n*-butyl ketone	0.052	0–8*M*	0.101	0–6*M*	0.106	0–6*M*	0.125	0–2*M*
Methyl *n*-amyl ketone	0.066	0–8*M*	0.110	0–2*M*	0.149	0–6*M*	0.165	0–2*M*
Methyl *n*-hexyl ketone	0.085	0–8*M*	0.152	0–2*M*	0.193	0–4*M*	0.219	0–2*M*

TABLE III

ELUTION DATA OF KETONES ON DOWEX-50-X8, HYDROGEN FORM, 200–400 MESH

	C					*Negative slope of log C vs. M plot*	*Extent of linearity of log C vs. M plot*
Molarity of methanol	0.0	2.0	4.0	6.0	8.0		
Acetophenone	15.3	12.1	9.56	7.25	4.94	0.054	0–6*M*
Methyl iso-butyl ketone	3.76	3.21	2.76	2.32	1.95	0.035	0–8*M*
Methyl *n*-heptyl ketone	24.7	17.1	11.6	8.24	4.60	0.085	0–6*M*
Methyl *n*-octyl ketone	52.5	33.6	21.3	12.7	6.93	0.100	0–6*M*
Methyl *n*-nonyl ketone	104	63.1	39.6	22.9	11.3	0.119	0–6*M*

TABLE IV

DISTRIBUTION RATIOS, C, ON DOWEX-1-X8, BROMIDE FORM, 200–400 MESH

Molarity, tetraethylammonium bromide	0.00	0.875	1.25	1.75	2.50	3.50
Methyl iso-propyl ketone	3.35	2.91	2.88	2.97	3.10	4.69
Methyl *n*-propyl ketone	4.42	3.79	3.54	4.06	4.33	6.58

SEPARATION OF MIXTURES

To demonstrate the applicability of solubilization chromatography to mixtures of higher ketones, the separation shown in Fig. 2 was performed.

A synthetic mixture of 0.2 mmole of each of seven methyl ketones was separated with the conditions and eluent changes indicated. Use was made of the data in Tables I and III to calculate[10,4] the most efficient sequence of eluent concentrations to be used. The calculated positions of the peaks for the ketones were 202, 256, 353, 506, 673, 836, and 950 ml as compared to the actual U^* values of 192, 255, 363, 519, 696, 861, and 923 ml.

The only ketone studied which was not included in the separation was acetophenone. Under the given conditions it would have been eluted between the peaks of methyl *n*-hexyl and methyl *n*-heptyl ketones, partially overlapping the former.

Although aliphatic alcohols containing more than nine carbon atoms did not give satisfactory elution graphs, it was possible to extend the ketone separation to include the eleven-carbon ketone, undecanone-2.

Methanol was chosen as the solubilizing eluent for the separation because the linearity and nonconvergence of the plots of log C *vs.* M through 8M (indicated in the eluent study) allowed greater latitude in changing eluent concentrations during the separation.

SALTING-IN CHROMATOGRAPHY

The fact that the ΔpH method of analysis for ketones could be carried out in salt solutions of varying concentrations allowed a study to be made of the chromatographic

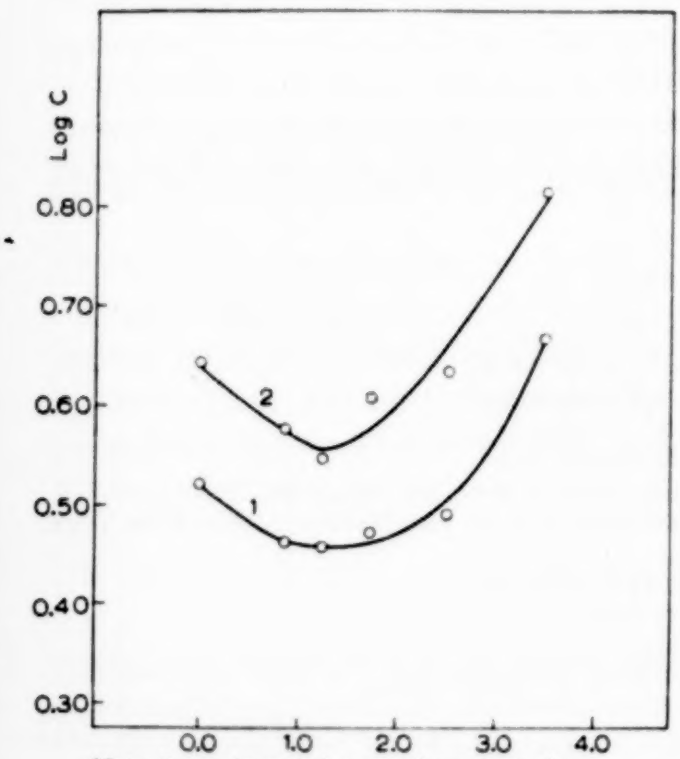

Fig 3. Plots of log C *vs.* M for two ketones. Dowex-1-X8, 200–400 mesh, bromide form.
1. methyl iso-propyl ketone
2. methyl *n*-propyl ketone

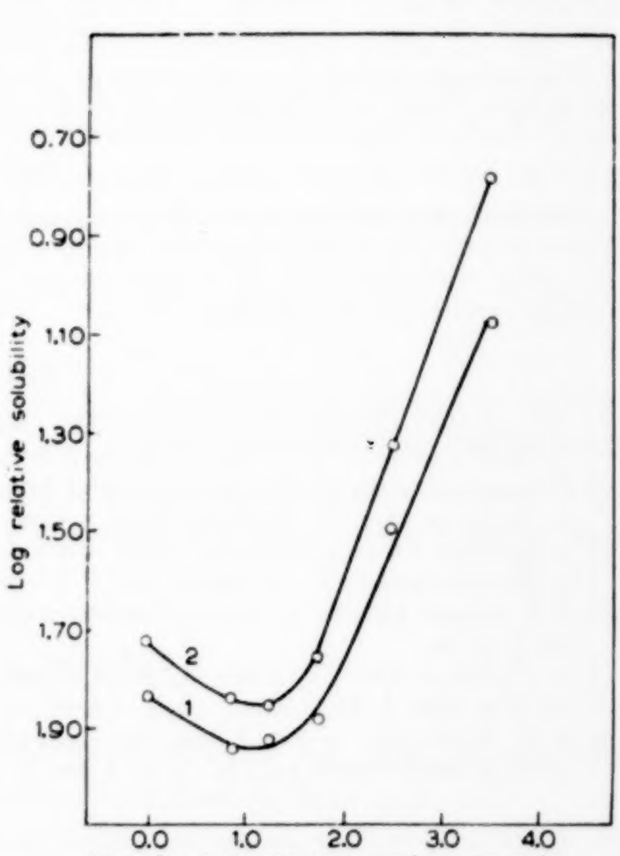

Fig. 4. Plots of the logarithm of relative solubility *vs.* M for two ketones in aqueous solutions of tetraethylammonium bromide.
1. methyl iso-propyl ketone
2. methyl *n*-propyl ketone

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behavior of the higher ketones with a salting-in salt, tetraethylammonium bromide, as eluent. It was hoped that the process of salting-in chromatography would follow the theory and equations of salting-out chromatography[1].

It was not possible to carry out such a study on Dowex-50 because the tetraethylammonium form of this resin has very little affinity for ketones. The C_o values, as calculated by equation (1), were: methyl *n*-butyl ketone, 0.688; methyl *n*-amyl ketone, 0.826; and methyl *n*-hexyl ketone, 0.917. This means that each appeared in the effluent almost immediately after the effluent volume equalled the interstitial volume. Similar results were obtained in elutions of acetone, methyl ethyl ketone, and methyl propyl ketone from Dowex-50 in the tetramethylammonium form.

Dowex-1-X8 in the bromide form was used subsequently to test the effects of tetraethylammonium bromide as eluent. Because Dowex-1 absorbs the higher ketones much more strongly than does Dowex-50, as was shown to be the case with the higher alcohols[5], two lower ketones (methyl iso-propyl ketone and methyl *n*-propyl ketone) were used. Table IV gives the results of the elutions. Plots of log C *vs.* M (Fig. 3) are very similar to plots of the logarithm of the solubility *vs.* M (Fig. 4), except that the slopes differ. In both cases, salting-in is observed at small concentrations of salt and salting-out at larger concentrations. Similar results have been found by SARMOUSAKIS AND LOW[11] for the effect of potassium thiocyanate on benzoic acid.

Salting-in chromatography apparently does not follow the theory of salting-out chromatography and would seem to be useless as a separation technique for organic compounds of large molecular weight.

ACKNOWLEDGEMENT

The authors express their gratitude to the Dow Chemical Company for financial support of this investigation and for the resins used in the work.

SUMMARY

The elution of ketones through ion-exchange resins with aqueous solutions of acetic acid or the lower alcohols as eluents has been studied. A mixture of seven ketones, the highest being undecanone-2, was separated by this technique. The elution of ketones with aqueous solutions of a salting-in salt was also studied.

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Received November 23rd, 1957

THE DIRECT MICRO DETERMINATION OF OXYGEN IN ORGANIC MATERIAL

by

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INTRODUCTION

The method proposed by SCHÜTZE[1] for the direct determination of oxygen, and adapted to the micro scale by ZIMMERMAN[2] and UNTERZAUCHER[3] needs little introduction. The sample is pyrolysed in a stream of pure nitrogen, oxygen is converted to carbon monoxide by passing over carbon at 1120°C, the carbon monoxide is then oxidized by reaction with iodine pentoxide, and the determination completed by the assay of either the liberated iodine or the carbon dioxide formed during the reaction. Prolonged use of this method has led to the publication of several modifications designed to overcome the difficulties that have been encountered during the analysis of different types of organic material. This paper presents further modifications which have been found necessary, especially when the method is applied to large numbers of petroleum fractions and also to organic compounds containing sulphur. The decomposition of petroleum materials gives rise to large amounts of hydrogen in the pyrolysis gases, and also to sulphur compounds which may exceed oxygen compounds in quantity, and hence present difficulties. The modifications incorporated in this method have provided a solution to both of these problems without loss of general applicability to pure organic compounds.

The determination of carbon monoxide

Ideally, the iodine liberated during the oxidation of carbon monoxide by iodine pentoxide is a direct measure of oxygen in the sample, and as such is often determined by the LEIPERT method[4]. However, the quantity of hydrogen present in the pyrolysis gases from hydrocarbons reacts with iodine pentoxide to a small extent, according to the equation

$$I_2O_5 + 5\,H_2 \rightarrow I_2 + 5H_2O$$

Analysis of hydrocarbon waxes by this method gave between 1% and 3% oxygen, when carbon and hydrogen results accounted for more than 99%.

The gravimetric determination of carbon dioxide also gives a direct measure of the oxygen present, and is not subject to interference from other components of the pyrolysis gases. The sensitivity of the measurement is similar to that of the LEIPERT method, particularly with the micro weighing methods available today. Fully damped micro balances, and careful handling of absorption tubes (in suitably gloved hands) make the determination appreciably faster and much simpler than the volumetric procedure. Furthermore with the adoption of this technique the use of iodine pentoxide is no longer necessary. The preparation of iodine pentoxide is lengthy, and not always satisfactory. The reagent is photosensitive and some preparations become inactive after only short periods of use.

Experiments were therefore carried out to check the efficiency of copper oxide as an oxidant under the conditions of the method. This reagent, which is robust and readily available, has been found suitable for the oxidation of carbon monoxide as required in the determination. It is quantitatively used up, but the life of one filling is considerable. When required, a fresh tube containing copper oxide is readily inserted in the apparatus. Test results showing complete oxidation of organic compounds under these conditions are included in Table I.

TABLE I

OXIDATION OF ORGANIC COMPOUNDS IN A STREAM OF NITROGEN BY PASSAGE OVER HEATED COPPER OXIDE WIRE

	Carbon %w	
	Found	*Theory*
n-Heptane	84.0 84.8	84.0
Benzene	91.9 93.0	92.3
Ethanol	51.6 52.2	52.2
n-Octacosane	84.9 85.5	85.1

The analysis of compounds containing sulphur

Several modifications of the UNTERZAUCHER method which have enabled the oxygen content of certain types of sulphur-containing material to be determined without error have been published. These include the use of a liquid nitrogen cold trap[5–7] and/or alkaline absorbers to remove sulphurous components. Because the extent of interference has been found to differ from one compound to another, it may be assumed that the nature and amount of the sulphur compounds formed vary according to the type of material being pyrolysed. Among the sulphur compounds formed during pyrolysis are hydrogen sulphide, carbon disulphide and carbonyl sulphide. A cold trap will condense out carbon disulphide and carbonyl sulphide, and an alkaline absorber will retain hydrogen sulphide. Use of the cold trap is unwise because oxygen will be lost as carbonyl sulphide, and failure to absorb carbon disulphide or carbonyl sulphide in the alkaline absorber will give high results when these compounds are further oxidized. Results (Table II) show the errors that occur using this type of scavenging system. These errors are variable and become even more serious when the oxygen content is low and the sulphur content high.

The use of a tube filled with reduced copper oxide[8] has been found very suitable

TABLE II

ANALYSIS OF ORGANIC COMPOUNDS USING DIFFERENT ABSORBERS TO REMOVE INTERFERENCE FROM SULPHUR

Compound	*Scrubber*	*Oxygen %w*		
		Result	*Theory*	
Sulphanilic acid	Alkali	28.4 28.5 28.2	27.7	High
Sulphanilic acid	Alkali + cold trap	27.2 26.7 26.7		Low
Sulphosalicylic acid	Alkali	52.4 67.0	50.3	High
Sulphosalicylic acid	Alkali + cold trap	47.5 46.6		Low

for the complete removal of the sulphur compounds likely to be formed. The following reactions take place:

$$\text{(i)}\quad H_2S + \overset{900^{\circ}C}{2\,Cu} \rightarrow Cu_2S + H_2$$
$$\text{(ii)}\quad CS_2 + 4\,Cu \rightarrow 2\,Cu_2S + C$$
$$\text{(iii)}\quad COS + 2\,Cu \rightarrow Cu_2S + CO.$$

The water formed when hydrogen from (i) is oxidized is removed by bubbling through sulphuric acid before the gases enter the absorption tube. The carbon formed in (ii) is retained in the tube.

THE MODIFIED METHOD

The material is pyrolysed in a stream of pure nitrogen and the gases passed over carbon at 1120°C to convert the oxygen to carbon monoxide. The gases are scrubbed by passage through copper at 900°C, and the carbon monoxide then oxidized to dioxide with copper oxide at 650°C. The carbon dioxide is dried with concentrated sulphuric acid and calcium chloride, and determined gravimetrically in a Pregl tube.

The procedure has been tested with a variety of organic compounds and fractions from organic material, including many petroleum products. The operating blank is less than 0.1 mg carbon dioxide or 0.036 mg oxygen.

A selection of the results obtained is shown in Tables III-V.

TABLE III

ANALYSIS OF STANDARD COMPOUNDS

	Oxygen %w	
	Theory	*Found*
p-Nitro-aniline	23.2	23.2 23.4
Phenacetin	17.85	17.7 17.8
Sucrose	51.4	51.2 51.4

TABLE IV

ANALYSIS OF SULPHUR COMPOUNDS

	Sulphur	*Oxygen %w*	
		Theory	*Found*
Sulphonal	28.0	28.0	27.8 28.3
Dicyclohexylsulphoxide	15.0	7.5	7.5 7.7
Dicyclohexylsulphone	13.9	13.9	14.0 13.9

TABLE V

ANALYSIS OF OIL FRACTIONS

	C %w	*H* %w	*N* %w	*S* %w	*O* %w	*Total* %w
A	81.2	12.1	0.1	3.4	3.0 3.1	99.9
B	76.5	11.4	Nil	7.0	5.3 5.1	100.1
C	85.3	12.1	Nil	0.9	1.7 1.7	100.0

Apparatus

As shown diagrammatically in Fig. 1. It comprises three main sections, purification, pyrolysis, and absorption.

Purification

(a) Gas pressure regulator — 100-ml Drechsel washing bottle provided with a T-piece delivery tube extending to the bottom of the bottle, and fitting loosely in the neck to permit escape of excess gas bubbles.
(b) Pyrex tube, 1.5 cm diameter and 30 cm long, with B10 joint and side arm 3.5 mm diameter at the top and drawn to 3.5 mm at the base, and surrounded by electrical heating wire, capable of maintaining tube at 200°C.
(c) Rotameter 0–25 ml/min air at 15°C and 760 mm.
(d) Purification tube, 25 cm long and fitted with B24 ground glass joints.
(e) Two-way tap on B24 cone.

Pyrolysis

(f) Quartz pyrolysis tube, 60 cm long, fitted with joint, side arm 8 cm long, and beak 8 cm long; 30 cm of the tube are enclosed in an electric furnace capable of maintaining a temperature of 1120°C.
(g) B14 cone and tap.
(h) Two-way tap.
(i) Tube filled with soda lime (Carbosorb).
(j) Quartz tube 25 cm long enclosed in an electrical furnace at 900°C.
(k) Quartz tube 15 cm long enclosed in an electrical furnace at 650°C.

Absorption tubes

(l) and (m) Tube absorbers fitted with ground glass stoppers.
(n) Pregl type absorption tube and counterpoise.
(p) Mariotte bottle of 2 l capacity, with tap (o) in inlet tube.
(q) Stainless steel tubing 3 mm outside diameter.
(r) Impregnated rubber tubing, 1–2 mm bore.
(s) Calcium chloride guard tube.

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Reagents

(a) Nitrogen, oxygen-free.
(b) Copper oxide, wire form.
(c) Calcium chloride, 14–20 mesh.
(d) Soda lime (Carbosorb), 14–20 mesh.
(e) Finely pelleted carbon black, Spheron 3, 4, or 6 (Cabot Carbon Ltd. London).
(f) Quartz wool.
(g) Sulphuric acid, A.R. specific gravity 1.84.
(h) Cotton wool.
(i) Kronig cement. Mix together in the proportion of 1 :4 paraffin wax and colophony. Heat till molten, and pour into small cylindrical moulds. After cooling, the glass mould may be chipped away to leave a cement stick which is suitable for use.

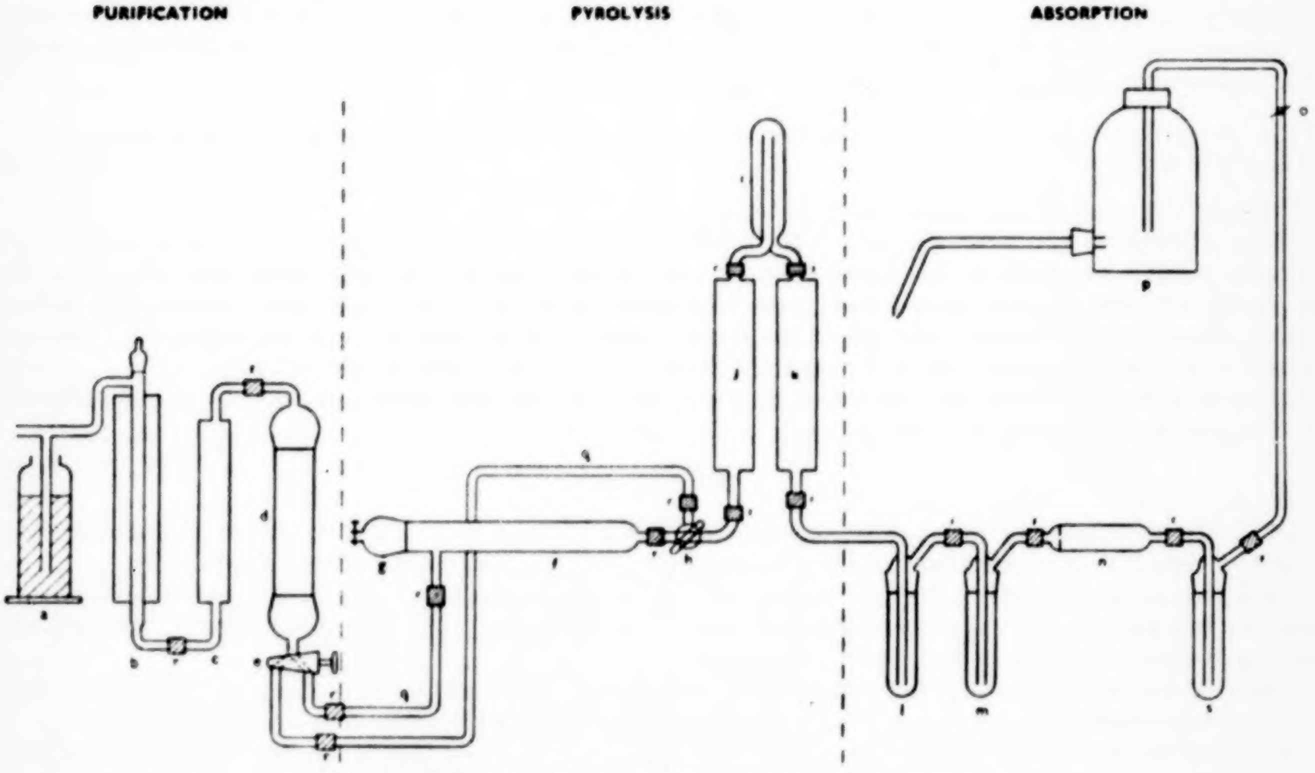

Fig. 1. The direct microdetermination of oxygen.

Preparation of apparatus

Clean all glass parts thoroughly, rinse with distilled water and dry.

Purification section

Fill Pyrex tube (b) with wire form copper oxide, warm the stopper, apply a thin film of Kronig cement, and seal into position. Connect the gas pressure regulator (a) to a hydrogen supply, and to the side arm of the pyrex tube, using stainless steel tubing and impregnated rubber tubing to make close-fitting connexions. Purge with hydrogen prior to raising the temperature of the copper tube to 200°C. Allow the water formed during reduction to escape at the base of the tube.

Fill the purification tube (d) as follows:

Seal the two-way tap into one of the joints with Kronig cement, add a plug of cotton wool and half fill the tube with calcium chloride. Add a further layer of cotton wool and fill the remainder of the tube with alternate layers of "Carbosorb" and cotton wool. Finish with a plug of cotton wool. Seal into position a B14 cone fitted to a short delivery tube leading to the top of the rotameter. When the copper oxide has been completely reduced discontinue the flow of hydrogen. Connect the exit end of the pyrex tube (b) to the base of the rotameter, and the top of the rotameter to the top of the purification tube, using stainless steel and impregnated rubber tubing. Connect the purification unit to the nitrogen supply.

Pyrolysis section

Place a small plug of quartz wool in the beak end of the pyrolysis tube and fill 28 cm of the tube with carbon. Hold in position with a further plug of quartz wool. This plug should fit just inside the furnace when the tube is in position.

Place the tube in position in the furnace and connect the sidearm to one of the tubes from the two-way tap at the base of the purification tube (d). Purge with nitrogen at the rate of 10 ml/min, and raise the temperature of the furnace to 1120°C.

Fill the 25-cm quartz tube (j) with copper oxide wire, and place in the 900°C furnace. Pass hydrogen through the tube and raise the temperature of the furnace to 200°C. Continue until complete reduction has taken place.

Fill the 15-cm quartz tube (k) with copper oxide wire and insert the tube in the remaining furnace. When reduction in the previous tube is complete, discontinue the flow of hydrogen, connect the tube to the two-way tap at the exit end of the pyrolysis tube, attach "Carbosorb" tube (i) and then connect the shorter tube containing copper oxide to the exit end of the "Carbosorb" tube. Raise the temperature of the reduced tube to 900°C and of the copper oxide tube to 650°C. Attach the tube (l) containing about 5 ml concentrated sulphuric acid, and follow it by a similar tube filled with calcium chloride (m). Continue to purge with nitrogen for some hours before use.

Connect the remaining arm of taps (e) and (h) together as in Fig. 1 using stainless steel tubing and impregnated rubber tubing connexions.

Absorption section

Prepare the absorption tube (n) as follows:

Place a small cotton wool plug next to the diaphram, and fill two-thirds of the tube with "Carbosorb". Insert a small cotton wool plug, fill the remainder of the tube with calcium chloride, and finish off with a small cotton wool plug. Warm the joint and seal the capillary end into position with a thin film of Kronig cement. Prepare the counterpoise tube by adding lead shot until its weight is a few milligrams lighter than the absorption tube. Seal in the stopper.

Connect the Mariotte bottle with tap (o) via a calcium chloride guard tube (s) to the absorption tube (n) as shown in Fig. 1.

Procedure

With nitrogen passing through the apparatus at the rate of 8–10 ml/min, insert the absorption tube between the two calcium chloride tubes, open tap (o) and purge with nitrogen.

Close tap (o), and turn taps (e), (h) and (g) in that order, so that nitrogen will escape through (g). Remove the tap and introduce the sample boat to a position 10 cm from the furnace, and replace the tap. Detach the absorption tube and weigh.

After replacing the absorption tube on the apparatus, continue reverse purging till a total time of 5 min has elapsed. Close tap (g), turn (e) and (h) in the forward direction and open tap (o).

Pyrolyse the sample in ten minutes, and continue purging for a further 10 min. During this time weigh the next sample.

After a total time of 20 min, close tap (o), reverse the nitrogen flow, introduce the next sample and weigh the absorption tube.

Procedure for sampling volatile liquids

(i) *Preparation of capillary weighing tubes.* Capillary tubes of length about 10 cm and bore 1 mm are suitable. Hold one end of a tube in forceps and draw the end to make a seal. Draw a fine capillary about 2.5 cm in length, making the bulb about 2.5 cm long. Cut the capillary in the middle. Repeat along the length of the tube.

Introduction of sample. Pour some of the test material into a sample phial and place in a 100-ml Buchner padded with cotton wool to keep the phial upright. Introduce the tapered end of a tared capillary into the liquid. Stopper the flask with a rubber bung containing a glass tap and apply suction from a water pump. When no further bubbles emerge from the sample, slowly open the tap in the neck of the flask. The capillary tube will then become filled with sample. Remove the capillary, centrifuge if necessary, carefully seal the end in a flame and reweigh.

A small air-pocket is retained in the open end of the tube after sampling and prior to sealing, but measurement of the volume of oxygen present has shown that an error of no more than 0.0005 mg carbon dioxide can result. This is less than the lowest recorded weight.

At the time of introduction of the sample into the pyrolysis tube break off the end of the capillary and introduce it supported in a platinum boat.

(ii) Liquids of low volatility may be weighed in a platinum boat without difficulty, but to prevent loss during the 5 min reverse purge, a cooling device should be placed around the part of the pyrolysis tube where the boat is situated.

Blank analysis

Carry out blank analyses using the procedure described but omitting the sample.

Cleaning the pyrolysis tube

With nitrogen flowing in the reverse direction, introduce a quartz tube into the front end of the pyrolysis tube. Pass air down the quartz tube using a very small air flow (*i.e.* the nitrogen rotameter must show a positive flow of nitrogen), and burn off the carbon attached to the tube. Move the burner gradually along the tube until all deposit had been ignited. Continue back sweeping with nitrogen for 5 min.

Calculation

$$\text{Percentage of oxygen} = \frac{36.35 \times (b-a)}{\text{sample wt. (mg)}}$$

where b = weight (mg) of CO_2 from the determination
a = weight (mg) of CO_2 from the blank.

ACKNOWLEDGEMENT

The author is indebted to the Directors of "Shell" Research Limited for permission to publish this paper.

SUMMARY

A procedure is described in which interferences caused by hydrogen and sulphur are eliminated. These occur when petroleum hydrocarbons or sulphur containing materials are analysed. Copper oxide, in conjunction with the gravimetric determination of carbon dioxide, has been found preferable to the iodine pentoxide procedure. The replacement of iodine pentoxide by copper oxide has also simplified the maintenance of the apparatus without any loss of applicability to organic compounds in general. Activated copper is used to absorb sulphur compounds. Details of the modified procedure are included.

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Received November 18th, 1957

SUCCINYL CHLORIDE AS A HYDROLYTIC REAGENT FOR THE DETERMINATION OF WATER

by

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INTRODUCTION

In the determination of carbon and hydrogen in organic compounds on the micro scale it is well-known that one of the principal sources of error lies in the weighing of the absorption tubes, and it is only by following a carefully standardised procedure for wiping and weighing that serviceable results can be obtained. The weighing operation is also the main delay in the rapid carbon and hydrogen method[1]; the combustion only takes 10 minutes, but the acclimatising of the tubes and both sets of weighings for the first determination, occupy the best part of an hour. It would be a great advantage if the weighing of the absorption tubes could be avoided, and the first simple alternative which suggests itself is the use of a titrimetric method. Such methods of completing the determination are not new and some of the early workers in the field of organic microanalysis addressed themselves to the problem, but very few critical studies of their recommendations have been made. At first sight, the main problem appears to be that of finding a reagent for the determination of water, for it would be expected that the determination of carbon dioxide could be readily accomplished by the use of standard barium hydroxide. Such a reagent for water would also have other applications outside the field of organic microanalysis, *e.g.* for the determination of water in gases, inorganic hydrates and many other substances.

LINDNER[2] has undoubtedly contributed most to present knowledge of this problem. Initially, he recommended α-chloronaphthyl dichlorophosphine oxide as a suitable reagent[2] to react with the water vapour evolved in the combustion; the hydrochloric acid formed, together with the carbon dioxide, was collected in standard barium hydroxide, which was then back-titrated. In a later publication LINDNER[3] preferred the unsubstituted naphthyl derivative as the reagent for water and he used two absorption vessels to collect the acid gases. The first contained water to absorb the hydrochloric acid, and the second barium hydroxide to remove carbon dioxide from the gas stream. Reagents for the determination of water have also been recommended by BELL[4], who used α-naphthoxydichlorophosphine, and by KUNZ[5] who used the oxide of this compound. VAN NIEUWENBURG[6] suggested cinnamoyl chloride as a suitable reagent. LINDNER[2] also examined phosphorus pentachloride and pentabromide and the double compounds formed from aluminium chloride/phosphorus pentachloride, chromium trichloride/phosphorus pentachloride and antimony pentachloride/phosphorus pentachloride as possible reagents for the determination of water. These last named inorganic compounds are all unsuitable because of their volatility or instability. All the organic compounds which have been recommended have one main disadvantage: they release the hydrochloric acid formed in the hydrolysis vere slowly. Hence, the time required to complete a determination is too long and the well-established gravimetric procedure has usually been preferred. The present paper describes an attempt to find a new reagent for the determination of water. The ideal properties of such a compound are briefly summarised below.

(1) It should react quantitatively and stoichiometrically with water to give a product which can be collected and determined by titrimetric means. (2) Such a reagent should be relatively non-volatile. (3) It should react instantaneously with water and should be capable of releasing the volatile product of the reaction immediately. (4) The nature of the reagent and the hydrolytic product should be such that they do not interfere with the determination of the carbon dioxide.

REAGENTS EXAMINED

In the initial stages of the investigation the selection of the reagents to be examined was largely governed by considerations of commercial availability and cost. Nevertheless the range was made as representative as possible; the following compounds were examined:

Antimony(III) chloride
Arsenic(III) chloride
Titanium(IV) chloride
Zirconium(IV) chloride
Aluminium chloride
Ethyltrichlorosilane
n-Propyltrichlorosilane
Triphenylchlorosilane
α-Naphthoxydichlorophosphine
Cinnamoyl chloride
p-Toleune sulphonyl chloride
Butyryl chloride
Trichloroacetyl chloride
Succinyl chloride

Of the inorganic compounds which were tested as possible reagents, none proved to be suitable. They all reacted slowly in varying degrees at low temperatures; although elevation of temperature accelerated the reactions, the corresponding increase in the blank values, owing to increased volatility, made them unsuitable as reagents. These results are similar to those obtained by LINDNER[2] with other inorganic compounds, and so it may be concluded that it is improbable that a hydrolytic reagent for the determination of water will be found amongst the members of this class of compound.

Two liquid organosilicon chlorides were examined during the investigation, *viz.* ethyltrichlorosilane, and *n*-propyltrichlorosilane, but they were very volatile and gave high blank values. Moreover, the hydroxy compounds produced during the hydrolysis deposited on the walls of the apparatus and caused blockages unless extreme care was taken. These deposits formed water-repellent layers and there was the disadvantage that glass coated in this way became devitrified when heated. The solid triphenylchlorosilane was also tested; it gave a lower blank value, but the speed of the hydrolysis was slow.

At elevated temperatures the increased volatility made the reagent useless. It is possible that a suitable reagent might be synthesised from this range of substances, but no such work was attempted during the present investigation.

A selected range of organic acid halides was next examined. Bell's reagent, *α*-naph-

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thoxydichlorophosphine, was re-tested. However, the commercial samples available proved to be extremely impure[7]. No further tests were done with this reagent.

Cinnamoyl chloride was examined as proposed by VAN NIEUWENBURG[6]. The reagent was maintained at 65–70°C, an oxygen flow rate of 17–18 ml/min was used and a determination was completed in one and a half hours. The blank values varied between 0.45–0.53 ml of 0.05*N* borax. A set of representative results using hydrated barium chloride is shown in Table I.

TABLE I

$BaCl_2.2H_2O$ (mg)	*Water calc. (mg)*	*Water found (mg)*	*Error (mg)*
22.263	3.28	3.29	+0.01
30.768	4.54	4.51	—0.03
23.145	3.41	3.43	+0.02
25.158	3.71	3.72	+0.01
8.617	1.27	1.27	±0.00
16.398	2.42	2.44	+0.02
21.198	3.13	3.07	—0.06

These values are somewhat better than those quoted by VAN NIEUWENBURG whose maximum error was 0.090 mg. He stated that the anhydride was formed in the reaction and the above results were calculated on this assumption. Attempts were made to decrease the total time of a determination by increasing the flow rate, but it was found that one hour was the minimum time required for complete evolution of the hydrochloric acid and that the optimum flow rate was in the region of 25–30 ml/min. At higher flow rates the results were low, presumably due to incomplete hydrolysis.

p-Toluene sulphonyl chloride was next examined, but it proved to be unstable as well as very volatile at 110°C and at lower temperatures the reaction rate was much too slow. Consequently this reagent is unsuitable.

Butyryl chloride and trichloroacetyl chloride were both examined, but they yielded variable and high blanks because of their volatility.

The most successful reagent examined was succinyl chloride. It is a colourless, pungent substance which melts at 17°C and boils at 192°C (760 mm pressure). It was tested at 60°C with a flow rate of 16–17 ml/min for one hour. A heating tape wound round the top of the inlet arm of the reaction vessel was maintained at 80°C to prevent premature condensation of the water vapour. Typical results are given in Table II. The blank values were higher than those of cinnamoyl chloride, but were constant for a particular batch of reagent, *e.g.* from 0.60–0.82 ml of 0.05*N* borax. Only one batch of cinnamoyl chloride was examined, so no information is available on the variability of the blanks with different batches of the reagent[8].

These results are similar to those obtained with cinnamoyl chloride, but the time taken to carry out a determation is somewhat less. They are calculated on the basis of anhydride formation as shown in the equation below.

$$(CH_2COCl)_2 + H_2O \rightarrow (CH_2CO)_2O + 2HCl$$

Under the conditions of the hydrolysis where a large excess of the acid chloride is present, formation of the anhydride may be expected. The optimum conditions for

TABLE II

$BaCl_2.2H_2O$ (mg)	*Water calc. (mg)*	*Water found (mg)*	*Error (mg)*
26.273	3.87	3.83	—0.04
42.969	6.33	6.38	+0.05
43.519	6.42	6.31	—0.11
30.014	4.43	4.49	+0.06
21.942	3.23	3.19	—0.04
40.520	5.97	5.94	—0.03
18.255	2.69	2.80	+0.11
33.168	4.89	5.08	+0.19

the use of this reagent were then determined and it was shown that at a flow rate of 50 ml/min, twenty minutes was the minimum time required to complete the combustion and the sweeping out of the hydrochloric acid. Blank values were still found to be consistent. A set of typical results is shown in Table III.

TABLE III

$BaCl_2.2H_2O$ (mg)	*Water calc. (mg)*	*Water found (mg)*	*Error (mg)*
37.338	5.51	5.76	+0.25
25.322	3.73	3.78	+0.05
32.685	4.82	4.83	+0.01
24.023	3.54	3.54	±0.00
18.950	2.79	2.80	+0.01
20.680	3.05	2.97	—0.08
19.118	2.82	2.76	—0.06

The slow combustion procedure is usually completed in one hour. The optimum flow rate to ensure complete evolution of the hydrochloric acid from the succinyl chloride in this time was found to be 10 ml/min.

EXPERIMENTAL

A selected range of acidic halides, both organic and inorganic, was examined using a conventional combustion train. Barium chloride ($BaCl_2.2H_2O$) was used as a source of water to test the reagents. The combustion apparatus, used with liquid reagents, is shown in Fig. 1.

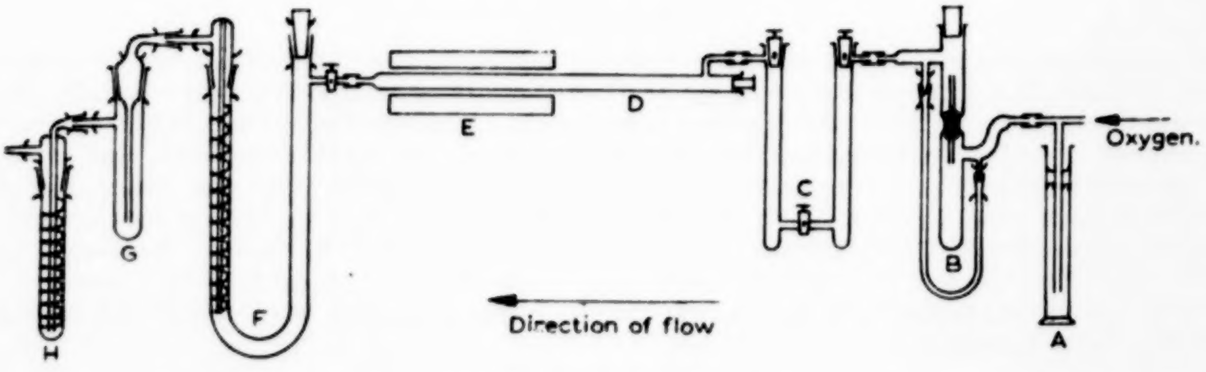

Fig. 1. The combustion apparatus. (A) Pressure head, (B) Flowmeter, (C) Scavenging tube, (D) Combustion tube, (E) Furnace [750 — 800°], (F) Reaction vessel, (G) Trap, (H) Absorption vessel.

Mercury was used to provide a head of pressure and the scavenging tube was charged with Anhydrone and soda asbestos in the usual way. Connections were made with impregnated rubber tubing or lubricated standard joints and steel springs. The reaction vessel (F), illustrated in Fig. 2, was adopted from a number of designs as being the most suitable owing to the fact that when it is heated, no water vapour condenses before it reaches the reagent, and because any moderate deposit does not block the gas flow. A liquid paraffin thermostat bath maintained the absorbers at elevated temperatures when necessary. When the bath was not used, a heating tape was used to prevent premature condensation of the water in the inlet arm of the reaction vessel. An ice/salt cooled trap (G) was included to retain any volatile impurities which might otherwise interfere with the determination. The water-containing vessel (H), as shown in Fig. 3, was used to absorb the acid gas evolved in the reaction. Solid reagents were used in the form of an intimate mixture with powdered glass, to prevent blockage of the tube. This mixture was packed into a Pregl absorption tube which was then used as a reaction vessel. When elevated temperatures were required, an electric aluminium heating block, controlled by a Simmerstat, was used to heat the Pregl tube containing the reagent.

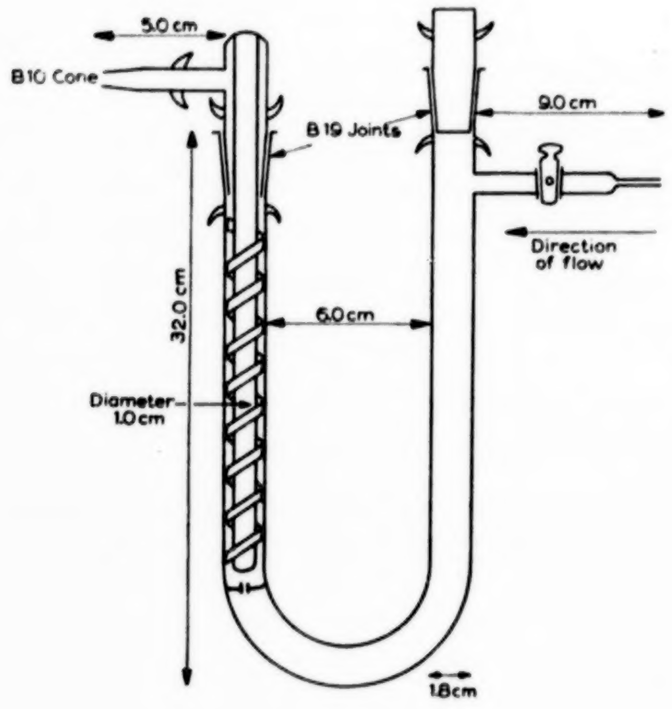

Fig. 2. The reaction vessel.

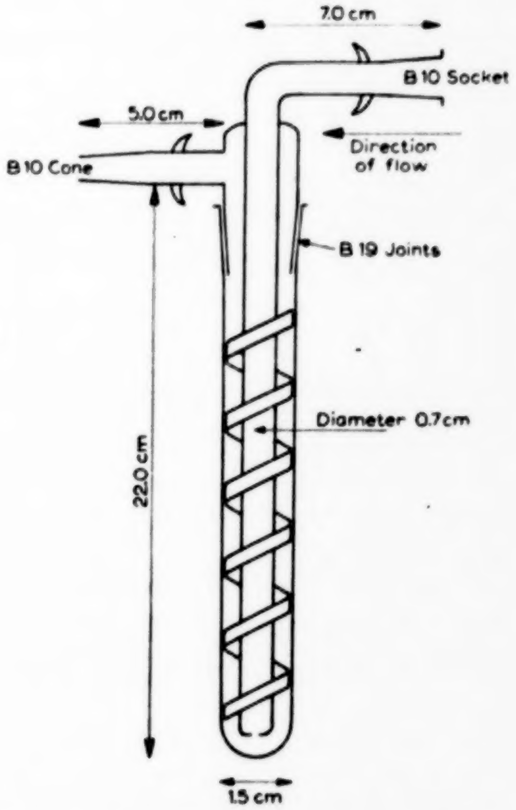

Fig. 3. Vessel for adsorption of HCl.

PROCEDURE*

The apparatus was assembled as above with the reaction vessel containing the reagent under test in position. When the furnace had attained the operating temperature (750–800°C) the train was swept out with oxygen at the required flow rate to condition the system before any analyses were carried out. The hydrated barium chloride, weighed into a platinum boat, was introduced into the combustion tube, dehydrated by heating with a bunsen, and the water was driven into the furnace over a period of 10 min. The apparatus was then swept out for varying times to remove all the acid gas from the reaction vessel into the absorber. At the end of a determination, the contents of the absorption vessel were carefully washed into a conical flask with water, and the acid was determined alkalimetrically using standard borax solution with a screened methyl red/methylene blue indicator.

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* The procedure used is designed to simulate the combustion conditions used in organic microanalysis. If the reagent is being used to determine *e.g.* hydrate water a much lower furnace temperature may be used and there is also no need to sweep out with oxygen.

DISCUSSION

Succinyl chloride has most of the properties required by a good hydrolytic reagent for water, but it is slightly volatile. This drawback is not serious, because a mean blank value usually accounts for all the slight variations. Under the recommended conditions the blank varies between 0.60–1.50 ml of 0.05*N* sodium borate for different batches of reagent. Although the blank varies with different preparations of the reagent, variation is slight within a particular batch.

The reaction which takes place is accelerated by increased flow rates. The results obtained have been calculated on the basis of the formation of the anhydride. This may be expected because under the experimental conditions a large excess of the acid chloride is present.

The results obtained indicate that succinyl chloride is a suitable reagent for the determination of moisture, particularly for the determination of hydrogen in the combustion of organic compounds. However, from the viewpoint of determining water *per se* a better reagent could probably be obtained by preparing some closely related compound which has a lower volatility, and which releases hydrochloric acid gas more readily. This possibility is now being examined.

ACKNOWLEDGEMENTS

We are indebted to the Department of Scientific and Industrial Research for financial aid in respect of this work.

SUMMARY

Several hydrolytic reagents have been examined for use in the titrimetric determination of water. Succinyl chloride was found to be satisfactory. It reacts more rapidly with water than cinnamoyl chloride. The reagent can be used under varying conditions of flow rate in a combustion apparatus and yields good recoveries of water.

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Received November 27th, 1957

THE SOLVENT EXTRACTION OF TRACE ANTIMONY(V)

by

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This investigation was carried out in order to learn more of the details relating to the solvent extraction of trace amounts of antimony(V) from aqueous hydrochloric acid solutions into various non-aqueous media.

INTRODUCTION

In 1911, MYLIUS AND HUTTNER[1] reported that antimony(V) in hydrochloric acid solution extracts into ethyl ether. In their experiments, the initial volumes of the two phases were equal, and the antimony(V) concentration was about 10 μg/ml. They stated that as the acid concentration in the aqueous phase increases from 0 to 20%, the antimony(V) extraction increases from 0 to 99%.

WARD AND LAKIN[2] have given an extraction procedure for the determination of trace antimony in soils and rocks. After solution has been effected, all of the antimony is converted to antimony(V) with the cerium(IV) ion. Isopropyl ether is then employed to extract about 90% of the antimony(V) from an aqueous solution which has been made from 1 to $2M$ in hydrochloric acid.

EDWARDS AND VOIGT[3] indicated that the extraction of antimony(V) with isopropyl ether becomes more effective as the hydrochloric acid concentration increases up to about $6M$. From about $6M$ to about $9M$ acid, the extraction is virtually complete, but above $9M$, it falls off rapidly.

BONNER[4] reports that the separation of antimony(III) and antimony(V) is feasible by using solvent extraction with isopropyl ether as the non-aqueous phase. He employed a radiotracer technique and found that in $6M$ hydrochloric acid solution about 98% of the antimony(V) goes into the ether phase.

NEUMANN[5] has investigated the ionic species of pentavalent antimony in hydrochloric acid solutions by using ultraviolet spectral data. He reported that the hexachloroantimonate(V) ion is present in acid concentrations of 10 to $12M$, the pentachlorohydroxoantimonate(V) ion in $8M$ acid, and the tetrachlorodihydroxoantimonate(V) ion is present in $6M$ acid. In solutions with lower acid concentrations, the more hydrolyzed ions are present.

EXPERIMENTAL CONDITIONS

Chemicals

The radioactive nuclide, antimony-124, was obtained in a high specific activity in the form of the chloride from The Oak Ridge National Laboratories. All organic solvents were C. P. Grade or better, and all inorganic compounds were Reagent Grade.

Apparatus

In all experiments, a temperature of 30.0 ± 0.5° was maintained. Water was pumped from a Sargent Constant Temperature Bath into a copper tray and then allowed to return to the bath. The copper tray was placed over 12 small magnetic stirring units which turned stirring bars placed in twelve 50-ml glass-stoppered Erlenmeyer flasks. The water level in the tray was always held just slightly below the tops of the flasks.

A Tracerlab Model SC-33 Scaler using a halogen-quenched Geiger tube was employed to measure the radioactivities of the samples, and a Beckman Model DU Spectrophotometer was used to make spectrophotometric studies. A null-type capacity meter was utilized in making the dielectric constant studies, and a Beckman Model H2 pH Meter was used for all pH determinations.

The ethyl ether system

A number of determinations of the amounts of hydrochloric acid solution and ethyl ether needed to produce equal volumes of 20 ml after equilibration were made. These experiments were conducted in glass-stoppered graduated cylinders which could be read to 0.1 ml. The results are presented in vertical columns 2 and 3 of Table I. For each of the combinations, the final acid normalities in the two phases were determined by titration with a standard solution of sodium hydroxide. These data appear in columns 4 and 5 of Table I. In each case, at least 4 determinations were made; the results were averaged for the final value. The last column in Table I, column 7, presents results obtained from measurements of the dielectric constant of the ether phase in each of the combinations.

The % antimony(V) extracted under various conditions are presented in column 6 of Table I. These data were obtained in the following manner. Into a 50-ml Erlenmeyer flask the amounts of hydrochloric acid solution and ethyl ether were added so as to give equal phases of 20 ml each when equilibrium had been obtained. Then enough of the radioactive antimony(V) solution was added so that the concentration in the original aqueous phase would be about 0.5 μg/ml. The stoppered flasks were then placed in the water bath and were allowed to stir for not less than two hours. After the stirring, the two phases were given at least two hours to separate. Three samples were taken from each phase with a 100-lambda pipet. These samples were deposited on glass planchets, evaporated to dryness, and then the radioactivities were determined. Averages were taken and the % extraction in each flask was calculated. Four such flasks were run at each acid normality, and these values were averaged to give the final % extraction.

Table II consists of data on a series of runs in which equilibrium volumes of 10 ml of aqueous phase and 20 ml of ethyl ether phase resulted. The technique followed the pattern of that given above

Table III presents the results of experiments carried out with equilibrium volumes of 20 ml of aqueous phase and 20 ml of ethyl ether phase. However, in these determinations various salts were added to the aqueous phase to see if they might affect the antimony(V) distribution. Columns

TABLE I

EXTRACTION OF ANTIMONY(V) IN THE ETHYL ETHER–HYDROCHLORIC ACID SYSTEM

(Final volumes of 20 ml ether: 20 ml acid)

Orig. acid N in water	*ml acid*	*ml ether*	*Final acid N*		*% Antimony extracted*	*Diel. constant of ether phase*
			in water	*in ether*		
0.00	18.2	22.2	0.00	0.00	0	6.5
0.10	18.2	22.2	0.09	0.00	0	6.5
0.30	18.2	22.2	0.28	0.00	0	6.5
0.50	18.2	22.2	0.46	0.00	1	6.5
1.00	18.2	22.2	0.91	0.00	1	6.5
2.00	18.2	22.2	1.82	0.00	2	6.5
3.00	18.2	22.5	2.73	0.00	2	6.5
4.00	17.9	23.1	3.58	0.00	17	6.5
5.00	17.0	23.7	4.26	0.00	51	6.5
6.00	16.0	24.6	4.81	0.00	56	6.5
7.00	14.3	26.6	5.01	0.00	43	6.5
8.00	12.4	28.8	4.97	0.00	33	6.5
10.00	9.9	31.7	4.96	0.00	18	6.5
11.93	8.4	33.0	4.95	0.00	9	6.5

2 and 3 show the data when the original acid normality was 3.00 and the salt concentrations at 0.1 *N* and 1.0 *N*. Columns 4 and 5 present the results when the original acid normality was 5.00 and the salt concentrations at 0.1 *N* and 1.0 *N*. None of these salts extracts to any appreciable extent into the non-aqueous phase[6].

Data were obtained on the spectra of antimony(V) in both phases after extractions involving final volumes of 20 ml of ethyl ether phase and 20 ml hydrochloric acid phase, but using an original concentration of 24 μg/ml of antimony(V) in the aqueous phase. Measurements were made at 5 mμ intervals from 235 to 400 mμ. The results obtained on the aqueous phases are given in Fig. 1, and those obtained on the ether phases are given in Fig. 2.

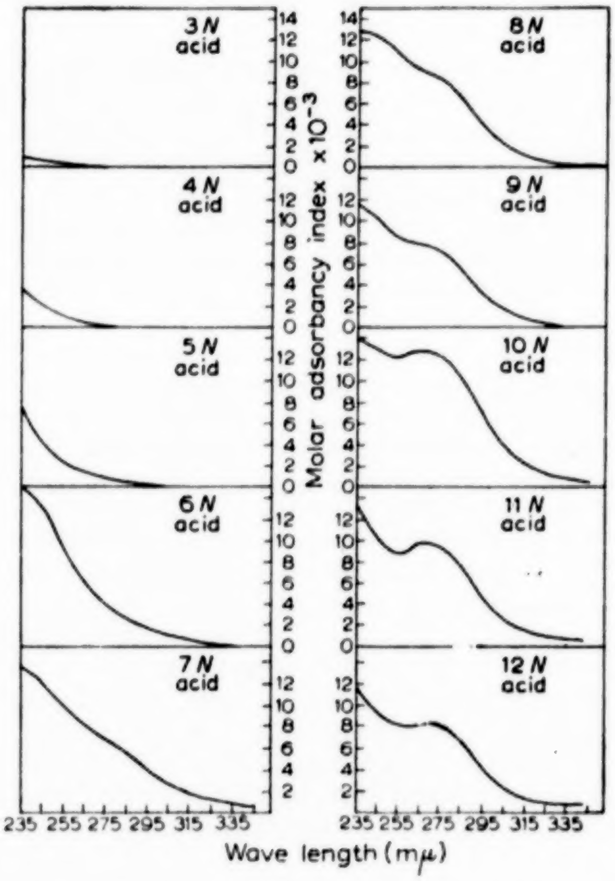

Fig. 1. Spectra of solutions of antimony(V) as a function of original acid concentration.

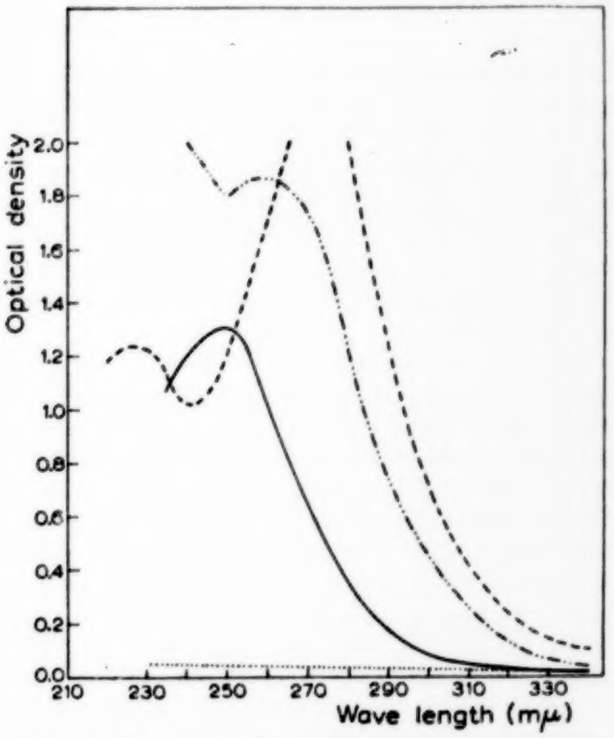

Fig. 2. Spectra of ether solutions of antimony(V) as a function of original acid concentration. ......, extracted from 2*N* acid; ———, extracted from 4*N* acid; —··—··, extracted from 6*N* acid; -----, extracted from 10/*N* acid.

Other systems

Table IV presents data on the isopropyl ether–hydrochloric acid system. This information was obtained from experiments similar to those described in the first two paragraphs of the previous section. In a like manner, Table V presents data on the isoamyl ether–hydrochloric acid system, Table VI presents data on the *n*-hexyl ether–hydrochloric acid system, and Table VII presents data on the chloroform–hydrochloric acid system.

DISCUSSION

Solubility studies

Columns 2, 3, 4 and 5 of Tables I, II, IV, V, VI, and VII present information regarding the mutual solubilities and the extraction of hydrogen ions into the non-aqueous phase in the various systems. For ethyl ether, the major effect seems to be the solution of ether in the aqueous phase; for the higher ethers (isoamyl, *n*-hexyl) it would appear to be the extraction of acid into the non-aqueous phase. In the cases of isopropyl ether and chloroform, both were of importance. These effects reflect the tendency of

TABLE II

EXTRACTION OF ANTIMONY(V) IN THE ETHYL ETHER–HYDROCHLORIC ACID SYSTEM

(Final volumes of 20 ml ether: 10 ml acid)

Orig. acid N in water	ml acid	ml ether	Final acid N		% Antimony extracted
			in water	in ether	
0.00	9.1	21.1	0.00	0.00	0
0.30	9.1	21.1	0.27	0.00	0
0.50	9.1	21.1	0.46	0.00	1
1.00	9.1	21.1	0.91	0.00	1
2.00	9.1	21.1	1.82	0.00	1
3.00	9.1	21.2	2.73	0.00	3
4.00	8.9	21.5	3.56	0.00	32
5.00	8.6	21.9	4.30	0.00	61
6.00	8.0	22.5	4.80	0.00	90
7.00	7.2	23.3	5.04	0.00	82
8.00	6.2	24.4	4.96	0.00	70
10.00	4.9	25.7	4.90	0.00	49
11.77	4.2	26.5	4.94	0.00	31

TABLE III

SALTING-OUT EFFECTS ON THE EXTRACTION OF ANTIMONY(V) IN THE ETHYL ETHER–HYDROCHLORIC ACID SYSTEM

(Final volumes of 20 ml ether: 20 ml acid)

Added salt	% Antimony extracted			
	Original acid N of 3.00		Original acid N of 5.00	
	0.1N salt	1.0N salt	0.1N salt	1.0N salt
None	2	2	51	51
LiCl	2	9	71	75
KCl	2	3	70	53
$MgCl_2$	2	7	68	79
$SrCl_2$	2	5	72	66
$AlCl_3$	2	12	68	68
$CuCl_2$	2	7	52	58
$ZnCl_2$	2	2	56	43

TABLE IV

EXTRACTION OF ANTIMONY(V) IN THE ISOPROPYL ETHER–HYDROCHLORIC ACID SYSTEM

(Final volumes of 20 ml ether: 20 ml acid)

Orig. acid N in water	ml acid	ml ether	Final acid N		% Antimony extracted	Diel. constant of ether phase
			in water	in ether		
0.00	19.5	20.5	0.00	0.00	2	3.6
1.00	19.5	20.5	0.99	0.00	81	3.6
2.02	19.5	20.5	1.99	0.00	94	3.5
3.00	19.5	20.5	2.91	0.00	98	3.5
4.00	19.5	20.5	3.96	0.00	97	3.5
5.05	19.5	20.5	4.93	0.00	99	3.4
6.05	19.5	20.5	5.86	0.05	99	3.4
7.06	19.3	20.8	6.71	0.11	99	3.4
8.08	18.3	22.0	7.26	0.18	98	3.3
9.00	16.0	24.2	6.97	0.27	95	3.3
9.93	13.5	28.6	6.41	0.30	79	3.2
11.00	11.6	30.6	6.11	0.32	48	3.2
11.85	10.3	31.7	5.76	0.35	16	3.1

TABLE V

EXTRACTION OF ANTIMONY(V) IN THE ISOAMYL ETHER–HYDROCHLORIC ACID SYSTEM

(Final volumes of 20 ml ether: 20 ml acid)

Orig. acid N in water	*ml acid*	*ml ether*	*Final acid N*		*% Antominy extracted*	*Diel. constant of ether phase*
			in water	*in ether*		
0.00	20.0	20.0	0.00	0.00	0	4.9
1.00	20.0	20.0	1.00	0.00	1	5.0
2.02	20.0	20.0	2.02	0.00	1	5.1
2.98	20.0	20.0	2.98	0.00	1	5.1
4.00	20.0	20.0	3.99	0.01	2	5.1
5.05	20.0	20.0	5.02	0.03	3	5.1
6.06	20.0	20.0	6.02	0.04	9	5.1
7.06	20.0	20.0	7.00	0.06	33	5.1
8.08	20.0	20.0	8.00	0.08	68	5.1
9.05	20.0	20.0	8.96	0.09	90	5.2
9.94	20.0	20.0	9.72	0.22	97	5.4
11.09	20.0	20.0	10.71	0.38	98	6.0
11.85	20.0	20.0	10.93	0.92	97	8.0

TABLE VI

EXTRACTION OF ANTIMONY(V) IN THE *n*-HEXYL ETHER–HYDROCHLORIC ACID SYSTEM

(Final volumes of 20 ml ether: 20 ml acid)

Orig. acid N in water	*ml acid*	*ml ether*	*Final acid N*		*% Antimony extracted*	*Diel. constant of ether phase*
			in water	*in ether*		
0.00	20.0	20.0	0.00	0.00	0	4.8
0.99	20.0	20.0	0.99	0.00	1	4.8
2.01	20.0	20.0	2.01	0.00	1	4.8
2.97	20.0	20.0	2.96	0.01	1	4.8
3.96	20.0	20.0	3.94	0.02	2	4.8
5.05	20.0	20.0	5.03	0.02	5	4.8
6.05	20.0	20.0	6.02	0.03	9	4.9
7.03	20.0	20.0	6.99	0.04	19	5.0
8.01	20.0	20.0	7.97	0.04	28	5.0
9.03	20.0	20.0	8.94	0.09	41	5.2
9.92	20.0	20.0	9.76	0.15	57	5.3
10.85	20.0	20.0	10.56	0.29	66	5.6
11.90	20.0	20.0	11.37	0.53	87	5.9

TABLE VII

EXTRACTION OF ANTIMONY(V) IN THE CHLOROFORM–HYDROCHLORIC ACID SYSTEM

(Final volumes of 20 ml chloroform: 20 ml acid)

Orig. acid N in water	*ml acid*	*ml chloroform*	*Final acid N*		*% Antimony extracted*
			in water	*in chloroform*	
0.00	20.9	19.2	0.00	0.00	0.0
1.00	20.9	19.2	0.99	0.05	0.3
2.00	20.9	19.2	1.96	0.13	0.3
3.00	20.8	19.3	2.95	0.17	0.5
4.00	20.8	19.3	3.95	0.21	0.5
5.00	20.8	19.3	4.92	0.28	0.7
6.00	20.8	19.3	5.83	0.41	1.0
7.00	20.8	19.4	6.80	0.48	1.4
8.00	20.7	19.5	7.73	0.55	1.7
10.00	20.6	19.6	9.67	0.63	1.9
12.06	20.4	19.8	11.61	0.69	2.4

ethers to participate in hydrogen bonding with the acid hydrogen and the idea that the lower-molecular-weight ethers tend to be more compatible with aqueous solutions than the higher ones.

Antimony(V) extractions

Column 6 in Tables I, II, IV, V, VI, and VII present the results of the extraction of trace amounts of antimony(V) from aqueous hydrochloric acid solutions into the various non-aqueous media. Isopropyl ether turns out to be the best extractant, with the most appropriate range running from an original acid normality of 3 to 9. Isoamyl ether is also effective at an original acid concentration of 11 *N*. A volume-ratio change in the ethyl ether system (as shown in Tables I and II) gives enhanced extraction, and probably indicates that such would be the case with the other systems.

Salting-out studies

The salting-out studies made in the ethyl ether system are presented in Table III. When the salts are at concentrations of 1 *N*, salting out seems to be the most pronounced for small, highly-charged cations, as would be expected. Some of the results in 5*N* acid are strange in that the extraction seems to decrease as the salt concentration increases (note potassium, strontium, and zinc). This behavior may be due to a combination of several effects including ionic interactions, but no simple explanation is apparent to the authors. In general, the presence of any salt tends to increase the extraction of the antimony(V).

Dielectric-constant studies

Dielectric constant data for the non-aqueous phases of some of the systems are presented in column 7 of Tables I, IV, V, and VI. In general, the changes in dielectric constant follow the extraction of hydrogen ion, as would be expected. Just why the isopropyl ether curve shows a slight decrease is not clear. Perhaps this is tied up with the reason why this ether acts so effectively as an extractant for the antimony(V).

Spectrophotometric studies

Ethyl ether and hydrochloric acid solutions containing antimony(V) were equilibrated to give equal volumes of the two phases. Spectrophotometric measurements were made on both phases and the data are presented in Figs. 1 and 2. NEUMANN[5] has shown that the wavelengths of maximum absorption for three antimony(V) species are as follows: 272 mμ for the hexachloroantimonate(V) ion, 251 mμ for the pentachlorohydroxoantimonate(V) ion, and 221 mμ for the tetrachlorodihydroxoantimonate(V) ion. When the original concentration of acid in the aqueous phase is 3, 4, or 5*N*, the curves in Fig. 1 indicate that the most prevalent form is the tetrachlorodihydroxoantimonate(V) ion. The curves for 6, 7, and 8*N* acid do not take the shape of any of the curves obtained by NEUMANN. The conclusion is that several of the species were present. The area under the curves and between 270 and 290 mμ for the 6, 7, and 8*N* plots seems to be increasing. This probably implies that the concentration of the hexachloroantimonate(V) ion is increasing.

The curves from 9 to 12*N* acid show a definite hump at 270 mμ. The general shapes of these curves can be obtained by adding curves for the hexachloroantimonate(V) ion and the tetrachlorodihydroxoantimonate(V) ion. This may indicate that the pentachlorohydroxoantimonate(V) ion is present only in relatively small amounts.

The data for the ethyl ether phases appear in Fig. 2. The small amount of antimony(V) extracted from the $2N$ acid would appear to be the more hydrolyzed forms. The curve obtained from the extraction of the $4N$ acid shows a definite hump at 250 mμ which probably corresponds to the pentachlorohydroxoantimonate(V) ion. The data for the extractions from the 6 and $10N$ acid give curves similar to the additive curve for the hexachloroantimonate(V) ion and the tetrachlorodihydroxoantimonate(V) ion. For the $6N$ acid, the latter seems to be more abundant, and for the $10N$ acid, the former appears to be more abundant.

CONCLUSIONS

From this series of studies, it is obvious that many factors may be involved in the extraction of a given oxidation state of an element from one liquid phase into another. It is often difficult to single out one factor as being the most important, and such is the case in this investigation.

One of the more significant factors observed in this study was the acid concentration. It appears that the species of antimony(V) as well as some salting-out effects were at least partially controlled by the hydrochloric acid concentration. In certain systems the acid concentration was also quite important with regard to the solubilities of the two phases in each other. In general, the isopropyl ether system appears to be the most suitable for the extraction of antimony(V).

Salting-out studies and investigations of the dielectric constants of the various non-aqueous phases both follow predicted trends.

In the ethyl ether system, the more hydrolyzed antimony(V) species are present in the aqueous phase when the original acid concentration is below $3N$. Very little antimony(V) is extracted under these conditions. From 3 to $6N$ original acid concentration, the amounts of the pentachlorohydroxoantimonate(V) ion and the tetrachlorodihydroxoantimonate(V) ion are increasing. At $6N$ original acid, the pentachlorohydroxoantimonate(V) ion appears to be the most abundant form. It is also to be noted that the maximum extraction occurs at this point. From 7 to $12N$ acid, the concentration of the hexachloroantimonate(V) ion is increasing while the pentachloroantimonate(V) ion is decreasing. The antimony(V) extraction is also decreasing. The ether phase appears to extract the more hydrolyzed species in very small amounts from the $2N$ acid. From the 4, 6, and $10N$ acid, the less hydrolyzed forms are being extracted. It seems that the tetrachlorodihydroxoantimonate(V) ion and the pentachlorohydroxoantimonate(V) ion are the most extractable species.

In the other ethers, it would seem that the pentachlorohydroxoantimonate(V) and the hexachloroantimonate(V) are the species that are probably extracting.

ACKNOWLEDGEMENT

The early stages of this research were supported by a grant from the United States Atomic Energy Commission, for which gratitude is expressed.

SUMMARY

An investigation of the extraction of trace amounts of antimony(V) from aqueous hydrochloric acid solutions into various ethers and chloroform has been carried out. Before extractions were made, mutual solubility studies of the two-phased systems were conducted. Then extraction experiments were performed using original aqueous acid concentrations from 0 to $12N$ and non-aqueous phases of ethyl ether, isopropyl ether, isoamyl ether, *n*-hexyl ether, and chloroform. Dielectric constant determinations were made in the equilibrated non-aqueous phases, and spectrophotometric and salting-out studies were carried out on the ethyl ether system. It was found that the isopropyl ether system presents the most advantageous conditions for the extraction of trace antimony(V).

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Received November 27th, 1957

ZIRCONYL-ALIZARIN BLUE S COMPLEX
A SPECTROPHOTOMETRIC STUDY

by

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DE BOER[1] noted that zirconyl salts gave a blue coloration with alizarin blue S. CHARLOT[2] reported on the stability of the lake at high acidities and developed a spot test for zirconium. The reagent may be utilised in the colorimetric estimation of the element. The colour reaction appears to be fairly specific. The lake shows an absorption peak at $600\ \mathrm{m}\mu$, and as little as $0.27\ \gamma$ of zirconia may be estimated or $0.025\ \gamma/\mathrm{cm}^2$ amounts detected.

EXPERIMENTAL

Reagent solution

0.1766 g of the dye (Hartman-Leddon and Co.) was dissolved in 1 l of 25% acetone to give a solution $3.536 \cdot 10^{-4}M$.

Zirconyl chloride solution

The zirconium solution was a sample available in the laboratory[3] and was standardized with mandelic acid[4]. A small quantity of hafnium was also present. A stock solution containing 0.04352 g/l or $3.536 \cdot 10^{-4}M$ was prepared.

Hydrochloric acid and sodium hydroxide were also of high purity.

Acetone, rendered aldehyde-free by standard procedure, was employed.

Instruments used

All absorption measurements were made with a Beckman model DU quartz spectrophotometer using a set of matched corex glass cells of 10 mm optical path. The cells were always oriented in the same direction. The light source was a hot-filament tungsten lamp.

Alizarin blue S though fairly soluble in water, separates out on keeping. The zirconium lake possesses similar characteristics. In 10% acetone the lake, however, is stable for a reasonable length of time, about 72 h. Higher concentrations of acetone up to 80% appear to have no effect on the properties of the lake.

The colour development is instantaneous and does not fade until the lake begins to separate out. The lake is also stable to high concentrations of hydrogen ions, but its complete formation takes a few minutes. The reagent becomes less absorbing as the acidity increases and this presents an additional advantage for colorimetric measurements.

Preliminary tests indicated that the acidity could be varied within wide limits between 0.2 to 0.7*N* in hydrochloric acid.

Optimum wavelength

Fig. 1 shows the absorbance curves of the reagent and zirconium complex in 0.5*N* hydrochloric acid in 10% acetone.

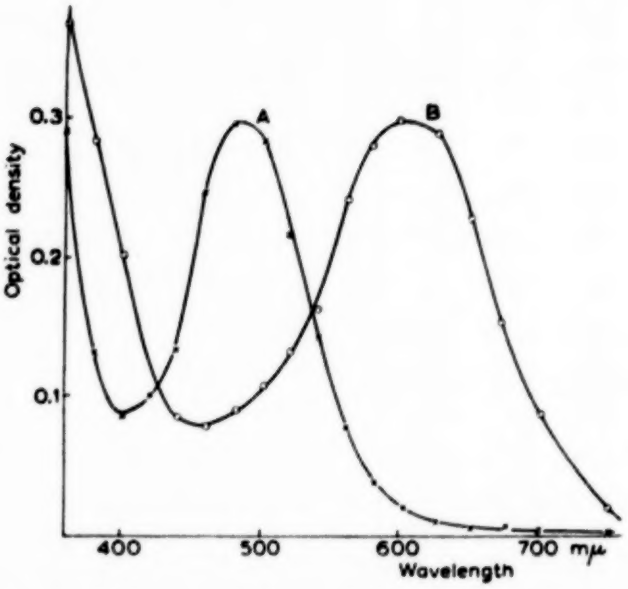

Fig. 1. Absorption characteristics of (A) 0.3532 mg of alizarin blue S, (B) lake from 0.3532 mg of reagent and 0.3432 mg of zirconia, in 10 ml solution.

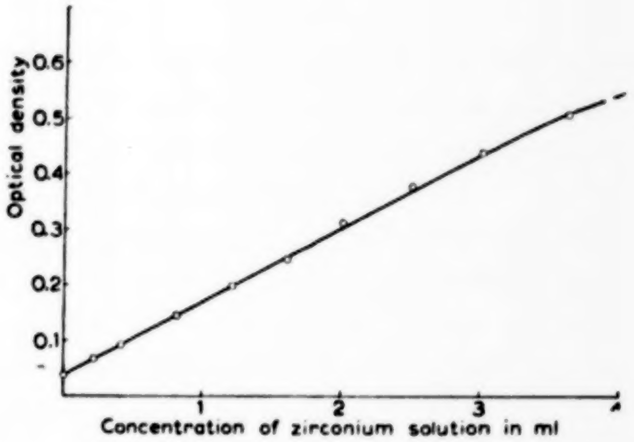

Fig. 2. Beer's law plot for the complex.

Estimation of zirconium

The dye obeys Beer's law at all wavelengths up to a concentration of 350 mg/l, a strength considerably above the concentration employed in these estimations. For the estimation of zirconium a working curve was obtained as follows: 4 ml of the alizarin blue S solution was complexed with varying amounts of the zirconium solution and made up to 10 ml with 0.5*N* hydrochloric acid in 10% acetone; after a lapse of 10 min, during which the colour of the lake was fully developed, the density of the resulting solution was measured against 0.5*N* hydrochloric acid in 10% acetone at 625 mμ (Fig. 2). Measurements may also be made at 600 mμ.

Interferences

Interferences from various cations and anions have been studied by adding known amounts of cations as chlorides and anions as their corresponding acids. The results are shown in Table I.

Oxalate, tartrate, phosphate should be absent. Even small quantities of fluoride present serious interference. Small amounts of sulphate are permitted. One mg of titania is also tolerated. Beryllium causes serious interference, the limit tolerated being 0.3 mg. Other tolerances are 292 mg of ThO_2, 200 mg of rare earth oxides, 6.0 mg of Al_2O_3, 70 mg of U_3O_8, 53 mg of CaO, and 20 mg of Fe_2O_3.

Estimation of zirconium in zircon

A sample of Travencore zircon was brought into solution following HOLENESS AND KEAR[5] and made up to 100 ml. One ml of this extract was diluted to 100 ml and aliquots

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TABLE I

INTERFERENCES BY DIFFERENT CATIONS AND ANIONS

Oxide or ion added	*Amount added in mg*	*Density*	*Amount of zirconia taken in γ*	*Amount of zirconia found in γ*
ThO_2	146.0	0.425	131	129
	292.0	0.296	87	85
	292.0	0.443	131	133
	365.0	0.545	131	167
Rare earth oxides	150.0	0.303	87	87
	200.0	0.307	87	89
	250.0	0.225	44	62
	250.0	0.481	131	149
Al_2O_3	6.0	0.163	44	42
	6.0	0.303	87	87
	15.0	0.545	131	167
U_3O_8	35.0	0.303	87	87
	70.0	0.167	44	43
	105.0	0.189	44	50
	105.0	0.487	131	148
Na^+	400.0	0.435	131	131
	800.0	0.410	131	122
Ca^{+2}	53.0	0.306	87	89
	53.0	0.431	131	130
	106.0	0.525	131	160
Fe_2O_3	20.0	0.310	87	90
	20.0	0.434	131	130
	40.0	0.266	87	80
	40.0	0.411	131	122
TiO_2	1.0	0.170	44	44
	1.0	0.306	87	89
	2.0	0.363	87	107
	2.0	0.537	131	163
SO_4^{-2}	2.0	0.302	87	87
	4.0	0.303	87	87
	6.0	0.221	87	70
$C_2O_4^{-2}$	0.4	0.424	131	127
	4.0	0.051	131	5
Tartrate	1.0	0.149	44	36
	1.0	0.367	131	108
Phosphate	0.8	0.141	131	35
	0.8	0.098	87	21

were complexed as before. The concentrations of zirconium were estimated by interpolating the densities of the complex at 625 mμ in the working curve, and compared with the result of a gravimetric estimation using tannin (Table II).

Composition of the complex

Job's method of continuous variation[6] applied to the zirconium–alizarin blue S lake in the acid range, indicated that the complex has the composition ZrOX (Fig. 3). The

TABLE II

ESTIMATION OF ZIRCONIUM IN ZIRCON

Weight of zircon sample decomposed = 0.4850g

Volume of zircon extract taken ml	*Density at 625 mμ*	*Weight of ZrO_2 computed in γ*	*Percentage of ZrO_2 (estimated)*	*Percentage of ZrO_2 in zircon (gravimetric)*
2.0	0.213	58.3	60.1	62.9
4.0	0.393	117.6	60.6	

composition, however, appears to vary with the concentration of the acid and in neutral solutions the complex tends to the formula $ZrOX_2$ where 'X' represents the dye ligand. The form of the JOB's curve, which does not present a sharp peak, indicates a certain degree of dissociation even in nearly neutral solutions, but this does not in any way vitiate the estimation of the element.

The conclusion with regard to the composition of the complex has been confirmed by employing the slope ratio[7] and molar ratio[8] methods (data not shown) and gravimetrically as shown below.

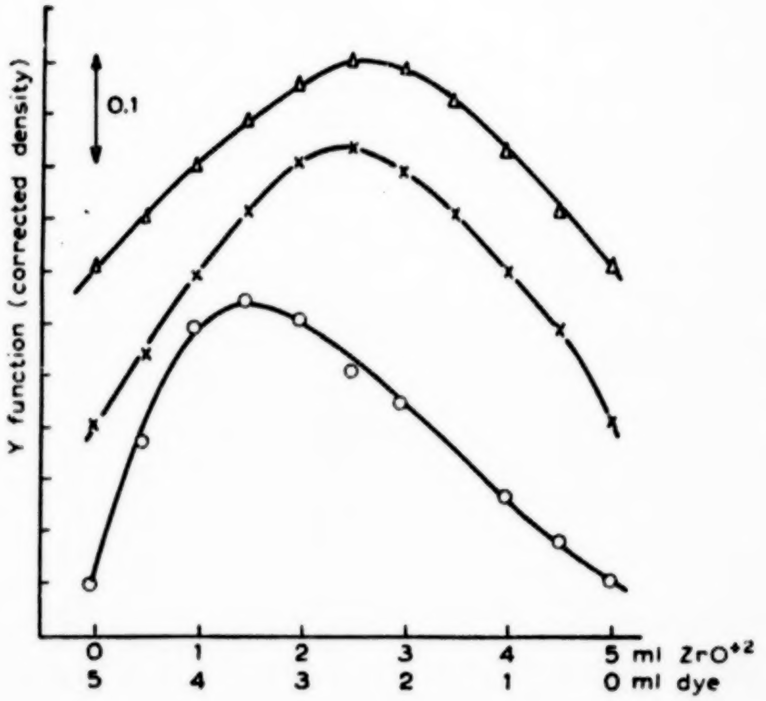

Fig. 3. JOB's method of continuous variation.
△ 1.0N HCl, × 0.5N HCl, ○ 0.01N HCl.

Gravimetric determination of composition. The complex was precipitated from aqueous solutions in 0.5N hydrochloric acid and after careful washing and drying at 100°, a known weight was ignited and the residue of zirconia was weighed (Table III).

A sample was further dissolved in 10% acetone and its absorption was found to be identical with the one prepared *in situ*.

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TABLE III

GRAVIMETRIC DETERMINATION OF THE COMPOSITION

Sample	*Weight of the complex*	*Weight of ZrO_2*	*Ratio of ZrO_2 to dye*
1	0.1900	0.0537	1 : 1
2	0.1431	0.0418	1 : 1

SUMMARY

Alizarin blue S in 0.5*N* hydrochloric acid and 10% acetone gives a coloured complex with zirconium salts, which is used for the estimation of zirconium. Measurements were made at 625 mμ and the interference of several cations and anions was studied.

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Received November 13th, 1957

ELIMINATION OF ANIONIC INTERFERENCE IN FLAME PHOTOMETRIC DETERMINATION OF CALCIUM IN THE PRESENCE OF PHOSPHATE AND SULPHATE

by

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INTRODUCTION

Flame spectrophotometry is becoming more and more important as a tool for the determination of small amounts of metallic elements in both inorganic and organic compounds, and its application is being extended to an ever wider range of materials.

The main limitation of the method is interference by other elements and ions with the emission of the element to be determined. Many ways have been proposed to counteract interference, all based on estimation of the extent of interference rather than on its elimination.

Usually, interference is estimated with the aid of comparative standards containing approximately the same amount of interfering elements as the sample to be analysed. This requires prior knowledge of the interfering elements in the sample[1,2].

The use of lithium as an internal standard[3] has the disadvantage of requiring special apparatus.

Spiking the sample with a known amount of the element to be determined[4] seems to be the most promising means for estimating interference, and may be applied without knowledge of the interfering element. However, in this method, the number of measurements required is high, and as they are done at a low emission grade, sensitivity is greatly reduced.

Particular difficulties are encountered in the flame photometry of calcium in the presence of phosphate or sulphate, which accompany it in most of the forms in which it occurs; both markedly lower the emission of calcium at its main characteristic wavelengths.

In the present work, the interference of phosphate or sulphate with the calcium emission is studied, and a method for the repression of this interference by the addition of certain cations is described.

EXPERIMENTAL

The following stock solutions were prepared:

(1) calcium chloride solution: 0.5 mg Ca^{+2}/ml
(2) phosphoric acid solution: 1.38 mg PO_4^{-3}/ml
(3) sulphuric acid solution: 2 mg SO_4^{-2}/ml
(4) lanthanum chloride solution ($LaCl_3 \cdot 7\ H_2O$): 6.6 mg La^{+3}/ml
(5) solutions of iron, magnesium and aluminium chlorides, each at a concentration of ∼ 2 mg/ml.

Measurements of the emission were carried out with appropriate quantities of the material in 25-ml samples. All samples were acidified with hydrochloric acid to pH 0.5–1.5 prior to analysis, preliminary tests having shown that variations of the acidity within this range do not influence the emission.

The emission measurements were carried out with a Beckman DU spectrophotometer. To increase sensitivity, two 10,000-MΩ resistors were connected in series in the load resistor box, instead of the usual single 10,000-MΩ resistor. The slit width was 0.15 mm and the selector switch was set to 0.1.

The instrument was calibrated to give a reading of 15 on the transmittance dial with a standard calcium chloride solution containing 20 μg Ca^{+2}/ml. The accuracy of measurement was to within ± 2% down to a calcium concentration of 5 μg/ml.

A red-sensitive phototube (No. 156) was used for emission at $\lambda = 622$ mμ and a U.V.-sensitive phototube (No. 2342/1) for $\lambda = 554$ mμ and $\lambda = 422.7$ mμ, these being the three wavelengths at which measurements were carried out.

The apparatus was provided with a battery power supply.

Hydrogen and oxygen pressures were regulated to 8 lb. H_2/sq.in. and 10 lb. O_2/sq. in. An atomizer provided with a medium bore was used.

RESULTS

The influence of phosphate on the emission of samples having a fixed calcium chloride concentration was determined.

It was found (Figs. 1, 2 and 3) that intensity of emission fell with PO_4^{-3} addition until the molar ratio of PO_4^{-3} to Ca^{+2} reached 1, when a constant emission was reached. Further addition of phosphate did not affect the emission any more. A similar observation has been described by TSUCHIHASHI AND SEKIDO[5]. The residual intensity of the emission in the presence of phosphate was found to be dependent on the calcium concentration of the sample.

The effect of addition of various cations (Mg^{+2}, Fe^{+3}, Al^{+3} and La^{+3}) to phosphate-

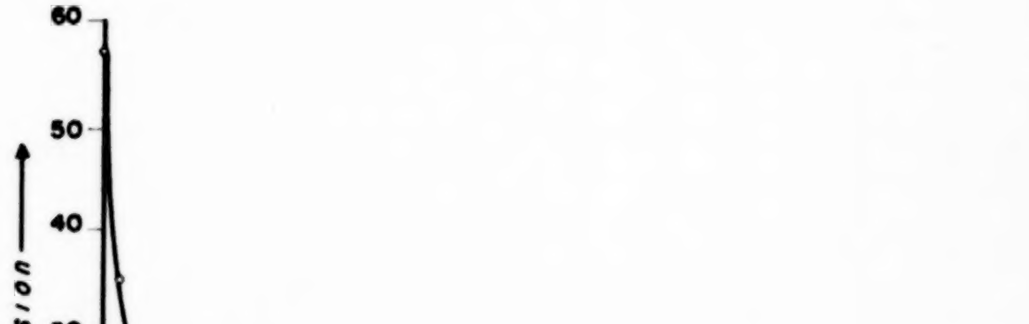

Fig. 1. Influence of phosphate on the emission of calcium.
$\lambda = 554$ mμ wavelength

●——● 30 p.p.m. Ca^{+2} + varying amounts of PO_4^{-3}
●——● 40 p.p.m. Ca^{+2} + varying amounts of PO_4^{-3}
○——○ 80 p.p.m. Ca^{+2} + varying amounts of PO_4^{-3}

containing calcium solutions was then investigated. Iron and lanthanum, when added in adequate amounts, were found to restore the intensity of emission to its original value. No effect of the other cations on the emission was observed. Partial elimination by calcium of the interference of sulphate and phosphate with the magnesium emission has been described by KNUTSON[6].

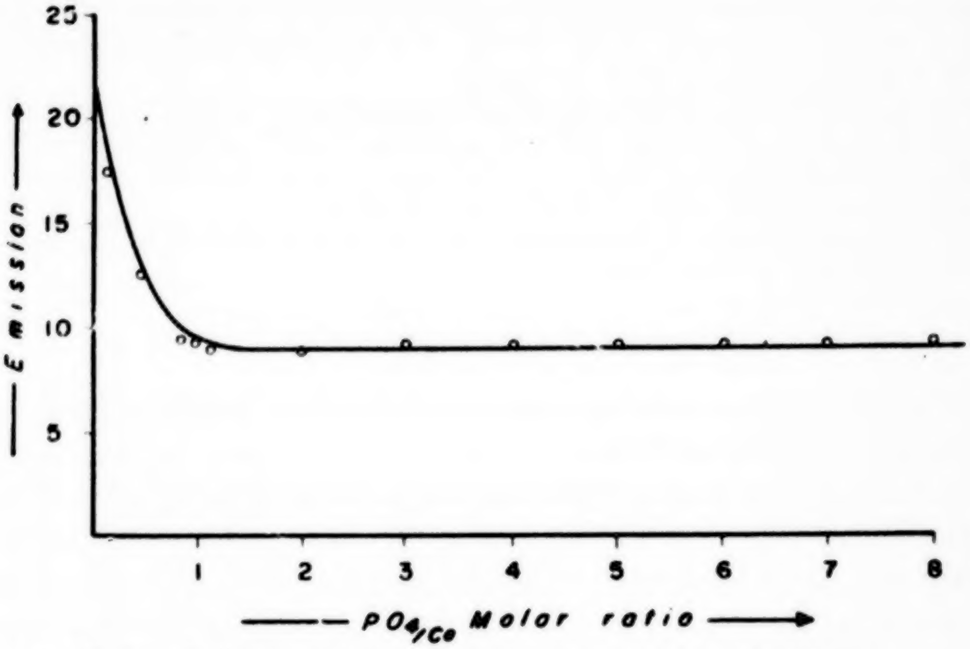

Fig. 2. Influence of phosphate on the emission of calcium.
$\lambda = 422.7$ mμ wavelength
o——o 30 p.p.m. Ca^{+2} + varying amounts of PO_4^{-3}

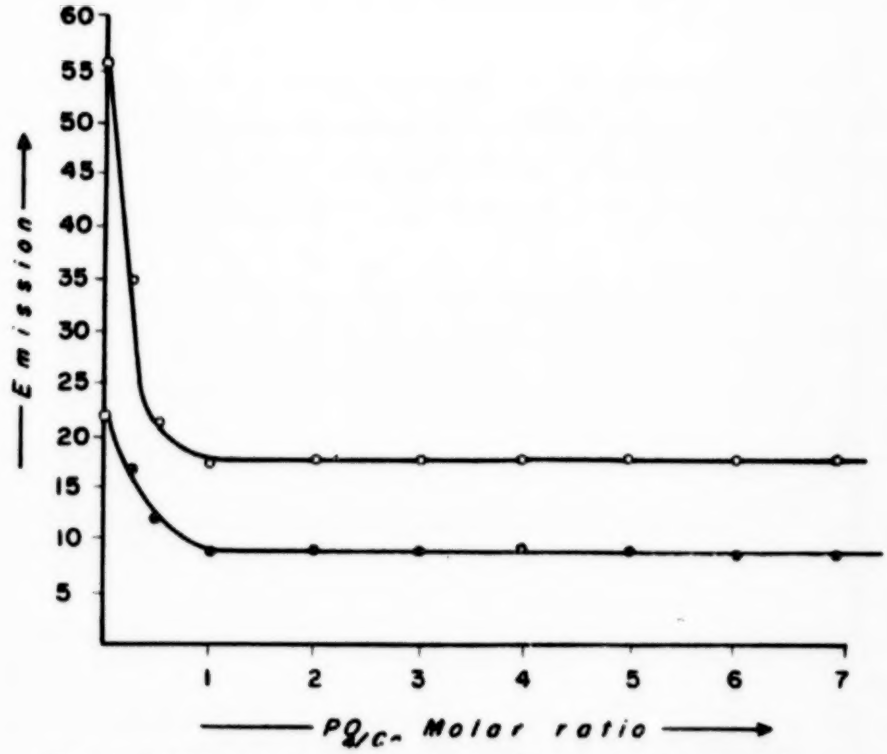

Fig. 3. Influence of phosphate on the emission of calcium.
$\lambda = 662$ mμ wavelength
●——● 30 p.p.m. Ca^{+2} + varying amounts of PO_4^{-3}
o——o 80 p.p.m. Ca^{+2} + varying amounts of PO_4^{-3}

Thus, when lanthanum is present in a molar ratio of $La^{+3}/PO_4^{-3} = 3.5:1$ to $4:1$, the original emission at wavelengths of $\lambda = 622$ mμ and $\lambda = 554$ mμ is restored. At $\lambda = 422.7$ mμ a molar ratio of 5:1 of lanthanum to phosphate is required for elimination of the interference (Figs. 4–7). It may be noted that lanthanum itself has no emission lines at these wavelengths.

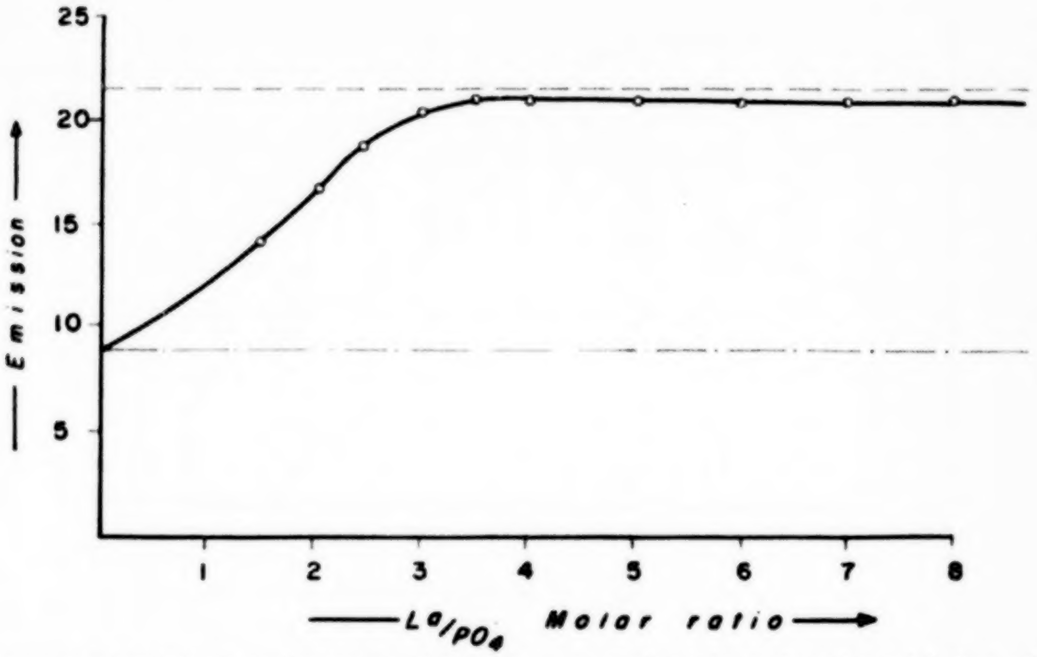

Fig. 4. Recovery of calcium emission in the presence of phosphate by the addition of increasing amounts of lanthanum.
$\lambda = 554$ mμ wavelength

— — — 30 p.p.m. Ca^{+2}
—.—. 30 p.p.m. Ca^{+2} + 71.5 p.p.m. PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$)
o——o 30 p.p.m. Ca^{+2} + 71.5 p.p.m. PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$)
+ varying amounts of La^{+3}

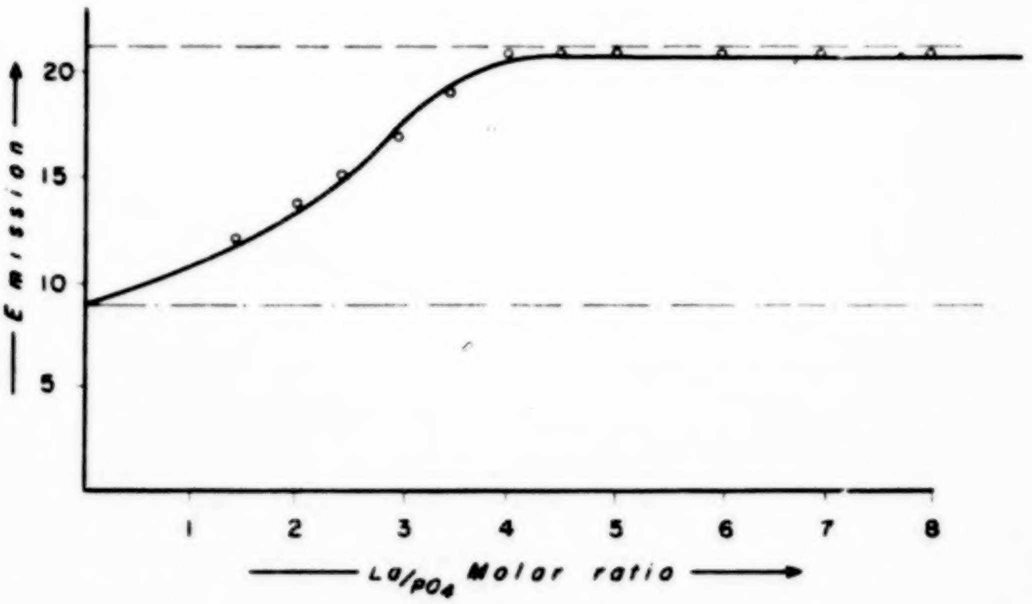

Fig. 5 Recovery of calcium emission in the presence of phosphate by the addition of increasing amounts of lanthanum.
$\lambda = 622$ mμ wavelength .

— — — 30 p.p.m. Ca^{+2}
—.—. 30 p.p.m. Ca^{+2} + 71.5 p.p.m. PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$)
o——o 30 p.p.m. Ca^{+2} + 71.5 p.p.m. PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$)
+ varying amounts of La^{+3}

Concerning the action of iron, a much larger molar excess — 16:1 of Fe^{+3} to PO_4^{-3} — is required for complete restoration of the intensity of calcium emission at $\lambda = 554$ mμ (Fig. 8).

Studies on the interference of sulphate gave similar results at $\lambda = 554$ mμ; thus,

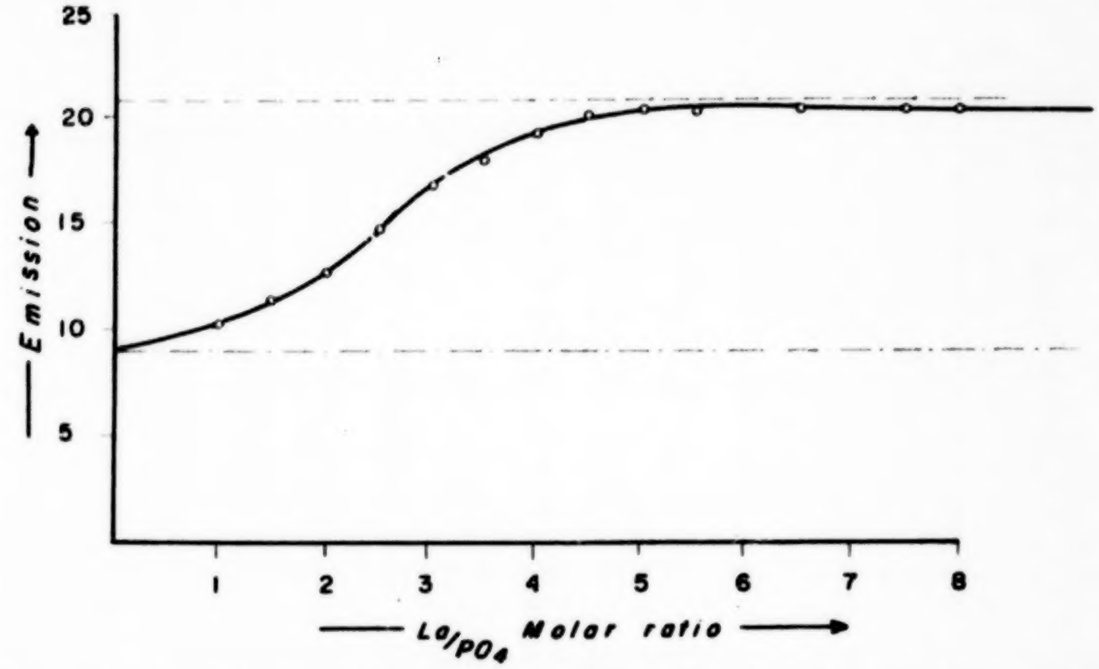

Fig. 6. Recovery of calcium emission in the presence of phosphate by the addition of increasing amounts of lanthanum.
$\lambda = 422.7$ mμ wavelength

— — — 30 p.p.m. Ca^{+2}
—.—. 30 p.p.m. Ca^{+2} + 71.5 p.p.m. PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$)
o———o 30 p.p.m. Ca^{+2} + 71.5 p.p.m. PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$)
+ varying amounts of La^{+3}

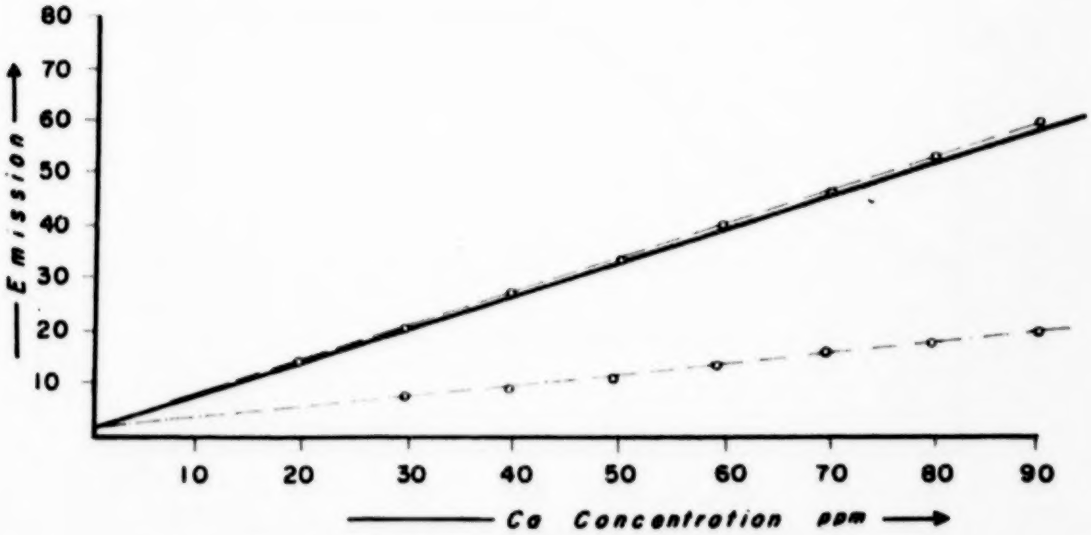

Fig. 7. Recovery of calcium emission in the presence of phosphate by the addition of lanthanum. Different concentrations of calcium.
$\lambda = 554$ mμ wavelength

— — — Ca^{+2}
—.—. Ca^{+2} + PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$)
o———o Ca^{+2} + PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$)
+ La^{+3} (Molar ratio $La^{+3}/PO_4^{-3} = 3.5$)

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constant emission was reached when the molar ratio of SO_4^{-2} to Ca^{+2} was 1.5 (Fig. 9), and addition of lanthanum at a molar ratio of 6–7:1 (La^{+3} to SO_4^{-2}) restored the intensity (Fig. 10).

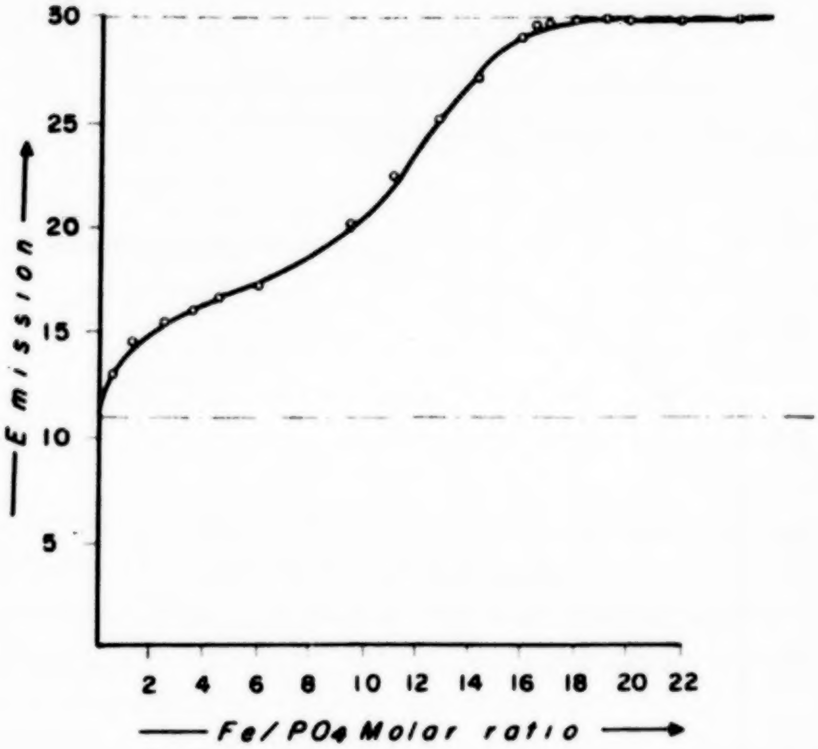

Fig. 8. Recovery of calcium emission in the presence of phosphate by the addition of increasing amounts of iron.
$\lambda = 554$ mμ wavelength

— — — 40 p.p.m. Ca^{+2}
—.—. 40 p.p.m. Ca^{+2} + 95.0 p.p.m. PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$)
o——o 40 p.p.m. Ca^{+2} + 95.0 p.p.m. PO_4^{-3} (Molar ratio $PO_4^{-3}/Ca^{+2} = 1$) + varying amounts of Fe^{+3}

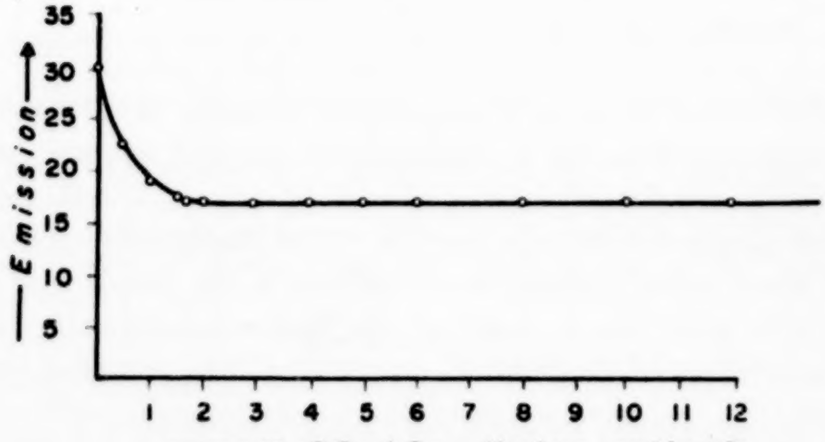

Fig. 9. Influence of sulphate on the emission of calcium.
$\lambda = 554$ mμ wavelength
o——o 40 p.p.m. Ca^{+2} + varying amounts of H_2SO_4

DISCUSSION

The reactions occurring in the flame in the calcium-phosphate mixtures are probably of the following form:

I . . . . $CaCl_2 + H_2O + E_1 \rightarrow CaO + 2\ HCl$

II . . . . $CaO + E_2 \rightarrow Ca + O$

III . . . . $2\ CaCl_2 + 2\ H_3PO_4 + E_3 \rightleftarrows Ca_2P_2O_7 + 4\ HCl + H_2O$

IV . . . . $Ca_2P_2O_7 + E_4 \rightleftarrows 2\,CaO + P_2O_5$

where E_1, E_2, E_3, and E_4, are heats of reaction.

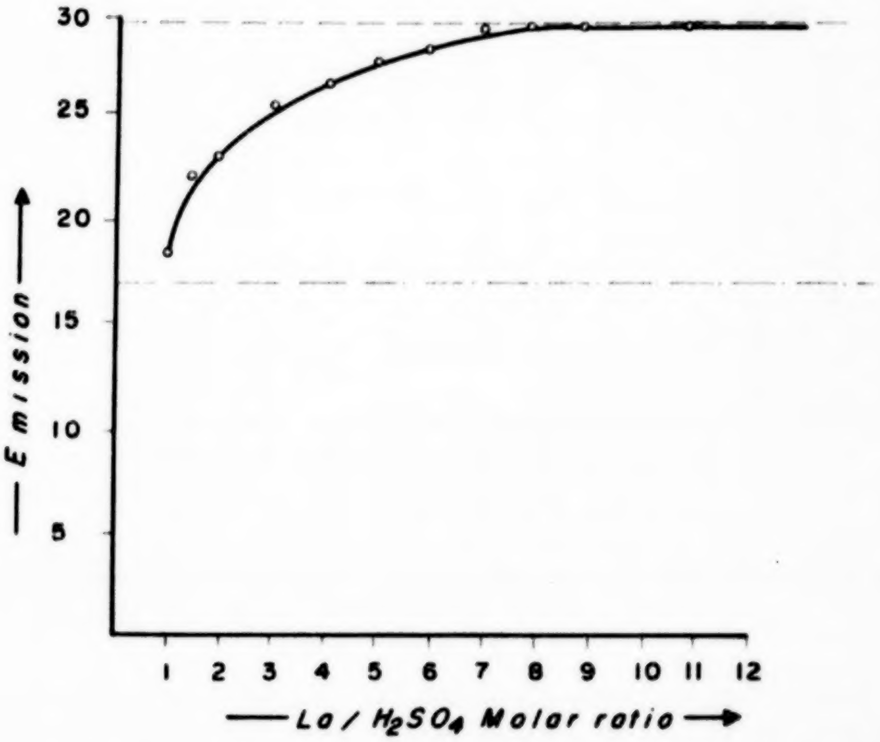

Fig. 10. Recovery of calcium emission in the presence of sulphate by addition of increasing amounts of lanthanum.

λ = 554 mμ wavelength

— — — 40 p.p.m. Ca^{+2}
—.—. 40 p.p.m. Ca^{+2} + 147 p.p.m. H_2SO_4 (Molar ratio $SO_4^{-2}/Ca^{+2} = 1.5$)
o——o 40 p.p.m. Ca^{+2} + 147 p.p.m. H_2SO_4 (Molar ratio $SO_4^{-2}/Ca^{+2} = 1.5$) + varying amounts of La^{+3}

Reactions I and II are those occurring in the absence of the interfering anions, it being generally accepted that the wavelengths of 622 and 554 mμ, are characteristic for CaO, that of $\lambda = 422.7$ mμ for Ca.

These reactions compete with III and IV, when phosphate ions (or sulphate ions) are present. The fixed residual emission of calcium in the presence of excess phosphate (due to reaction IV) probably depends on the flame temperature, which determines the degree of dissociation of the calcium pyrophosphate and thus the amounts of Ca or CaO formed.

When lanthanum is introduced into the solution, the following further reaction may occur:

III′ . . . . $LaCl_3 + H_3PO_4 + E_3' \rightleftarrows LaPO_4 + 3\ HCl$

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A similar equation would govern the reaction of iron ions.

From the heats of formation of lanthanum and calcium salts with various anions (Table I) it appears that $E_3' > E_3$, *i.e.* the phosphate of lanthanum is more highly thermostable than that of calcium. Thus in the presence of sufficient lanthanum, equation III′ entirely replaces III (plus IV), and all calcium chloride remains free to decompose into calcium oxide or calcium.

TABLE I

HEAT OF FORMATION OF SOME COMPOUNDS
(Data taken from the Critical Tables 1929)

Compound	*Heat of formation (E) kJ/gmole*
(1) $CaSO_4$	1405
(2) $Fe_2(SO_4)_3$	2685.8
(3) $La_2(SO_4)_3$	4131
(4) $Ca_3(PO_4)_2$	4110
(5) CaO	634
(6) La_2O_3	2100

It may be noted that reactions I, III, III′ occur in the lower, cooler part of the flame, while reactions II and IV occur in the hotter region.

It was found (compare Figs. 4, 5 and 6) that a somewhat higher ratio of lanthanum to phosphate is required to restore the intensity of the calcium emission at $\lambda = 422.7$ mμ than at $\lambda = 622$ or 554 mμ.

It has been shown previously that iron must be present in for greater excess than lanthanum for the complete recovery of the intensity of calcium emission. This may be explained as follows. The equilibrium in equation III′ depends obviously on the concentration of each of the components. As $LaPO_4$ is more stable than $FePO_4$, a higher surplus of ferric ions than of lanthanum ions is required to hold all the phosphate, and thus free all the calcium.

ACKNOWLEDGEMENT

This study has been carried out in the laboratories of the Israel Atomic Energy Commission, Analytical Division.

SUMMARY

Studies on the interference of phosphate and sulphate in the flame emission of calcium as calcium chloride have shown that there is a fall of intensity corresponding initially to the quantity of the interfering anion, the emission intensity reaching a constant value at a certain ratio of PO_4^{-3} or SO_4^{-2} to Ca^{+2}.

On addition of appropriate quantities of lanthanum (or iron) to the sample, the intensity of the calcium emission lines is restored to the value it had when the interfering anions were absent.

It is postulated that lanthanum replaces calcium in a phosphate- or sulphate-containing compound, that without lanthanum does not form calcium ions even at high temperature.

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Received November 24th, 1957

SOME EXPERIMENTS ON THE POLAROGRAPHY OF PLUTONIUM(VI) IN COMPLEXING MEDIA

by

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Use of the dropping mercury electrode for the polarographic reduction of any of the valency states of plutonium in non-complexing media is precluded by the values of the relevant formal oxidation potentials, which are +0.9 V and above[1]. (European Sign Convention). Two general approaches are possible, anodic polarography in non-complexing media using solid electrodes, or the use of complexing agents to preferentially complex the oxidised state and thus move the potential of the system into the working region of the dropping mercury electrode.

Rotating platinum micro-electrodes were used by HARVEY *et al.*[2] to determine the potential of the plutonium(III)/plutonium(IV) couple in 1*N* sulphuric, hydrochloric and perchloric acids. In the latter two acids, reproducible half-wave potentials could not be obtained. Using a similar technique, KEMP AND WEBBER[3] obtained an anodic oxidation wave for plutonium(III) in 1*N* hydrochloric acid at +0.66 V versus the saturated calomel electrode. For a particular electrode, repetition of the polarograms gave a successive decrease in wave height. This was attributed to the deposition of plutonium dioxide on the electrode surface, heating with aqua regia being necessary to restore the electrode to its original condition.

Available data concerning the polarography of plutonium in complexing solutions is apparently restricted to some quoted e.m.f. measurements[1] in acetate, mixed sulphate - fluoride and mixed sulphate - oxalate solutions.

The half-wave potential is related to the standard potential and concentrations of the reduced and oxidised species by the familiar equation:

$$E_{1/2} = E_o + \frac{2.303\,RT}{nF} \log \frac{C_{\text{ox}}\,f_{\text{ox}}}{C_{\text{red}}\,f_{\text{red}}}$$

where C and f represent concentrations and activity coefficients respectively. At 25° for a reduction involving one electron ($n = 1$) the half-wave potential is shifted by 0.059 V for every tenfold reduction of $C_{\text{ox}}\,f_{\text{ox}}/C_{\text{red}}\,f_{\text{red}}$. For the specific case of plutonium a shift of at least 0.7 V is required to bring the half-wave potential into the working range of the dropping mercury electrode, and it is therefore essential that the oxidised form be much more strongly complexed than the reduced form. Consideration of the aqueous chemistry indicated that such differences might be most readily manifest in the plutonium(VI)/plutonium(V) system. The polarographic reduction of plutonium (VI)in the presence of various complexing agents has therefore been examined.

EXPERIMENTAL

Apparatus and reagents

Polarograms were recorded using a Cambridge Pen Recording Polarograph and a dropping mercury cathode, the drop time of which could be conveniently varied within the range 3–5 sec. All solutions were degassed with cylinder nitrogen for 15–20 min prior to polarography, and solutions were maintained at 25° ± 0.5° using a small thermostatted bath.

Plutonium(VI) solutions were prepared at concentrations of 10–20 mg plutonium per ml by anodic oxidation of plutonium (IV) in $0.5N$ nitric acid. Details of the method and cell construction are given by HEALY AND GARDNER[4]. Analysis for residual plutonium (IV) was carried out chromatographically[5], or spectrophotometrically using the 475-mμ absorption peaks of plutonium (IV) and the 833-mμ peak of plutonium (VI). Each method indicated that the plutonium (VI) solutions employed contained less than 1% of plutonium (IV).

The absorptiometric studies on plutonium(V) in the presence of oxalate were carried out on a solution containing 2.7 mg/ml plutonium, using a Hilger Uvispek spectrophotometer.

RESULTS

Qualitative examination of the polarographic reduction of plutonium(VI) was carried out in a number of complexing agents, the results being summarised in Table I.

Of the waves recorded, only that in oxalate base was reversible.

TABLE I

Base electrolyte	*Pu(V) concentration*	$E_{\frac{1}{2}}$	*Reference electrode*
$1N$ sodium hydroxide	1 mg/ml	−0.89 V	Hg/HgO/NaOH
$0.1M$ sodium potassium tartrate	1 mg/ml	−0.5 V	Standard calomel
$1M$ acetic acid–sodium acetate pH 4.0	1 mg/ml	No wave	Standard calomel
$0.5M$ sodium oxalate–oxalic acid pH 4.0	1 mg/ml	−0.21 V	Standard calomel

Reduction of plutonium (VI) in sodium hydroxide base solution

This reduction was studied over the concentration range $0.1M$ to $1.0M$ sodium hydroxide. For a fixed concentration of plutonium the wave height decreases non-linearly as shown in Fig. 1. From 1.0 to $0.7M$ sodium hydroxide the observed reduction consists of a single wave having a half-wave potential of —0.90 V with respect to the mercury/mercuric oxide/sodium hydroxide reference electrode. On further decreasing the alkalinity to $0.68M$ sodium hydroxide, the reduction takes the form of two incompletely resolved waves of half-wave potential —0.86 and —1.13 V with respect to the same reference electrode. Fig. 2 (a) depicts this polarogram. On progressively reducing the alkalinity to $0.1M$ the double form of the wave is maintained but with rather poorer resolution.

These results suggest that irreversible reduction of one or more hydrolysed species of the plutonyl ion is occurring, the height of the waves being related to the concentration of the species, which will vary non-linearly with the hydroxyl ion concentration.

Reduction of plutonium (VI) in oxalate base solutions

To ensure maximum stability of the plutonium(V) state, reductions should be carried out in the pH range 3.5 - 4.5. pH 4.2 ± 0.1 was used for this work. The base electrolyte comprised sodium oxalate-oxalic acid of total concentration 0.18M. 0.1 ml of 0.1% proteose peptone was added as maximum suppressor, the total volume of polarographed solution being 5 ml. A typical polarogram is depicted in Fig. 2 (b).

Half wave potentials $E_{1/2}$ were calculated from the familiar equation:

$$E_{de} = E_{1/2} - \frac{0.059}{n} \log \frac{i}{i_d - i}$$

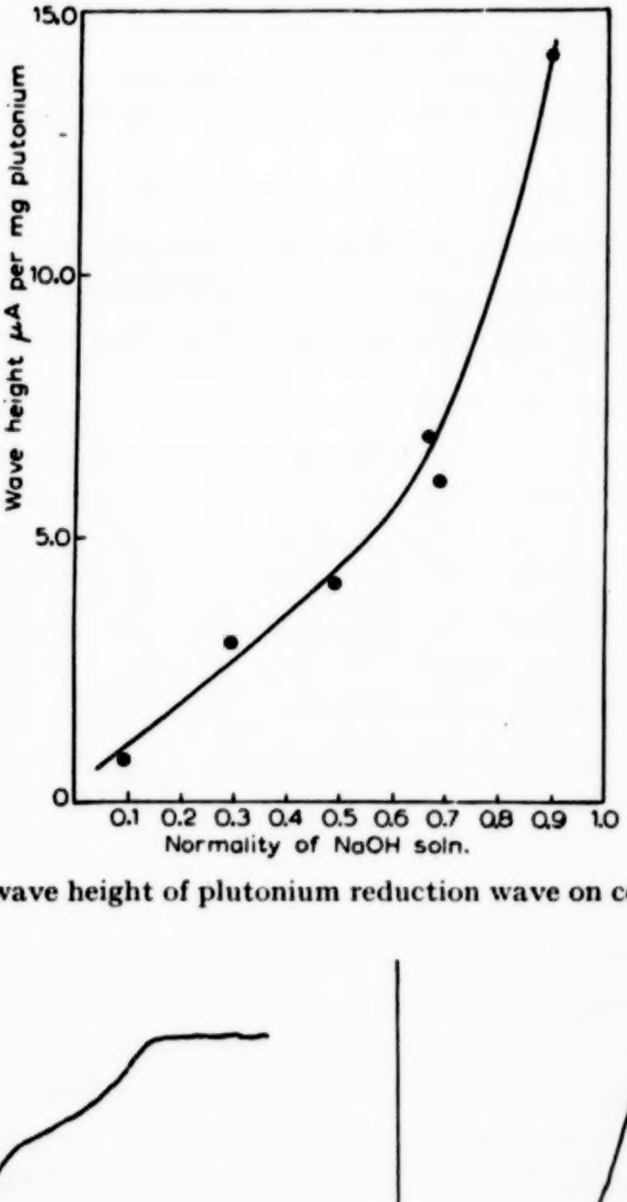
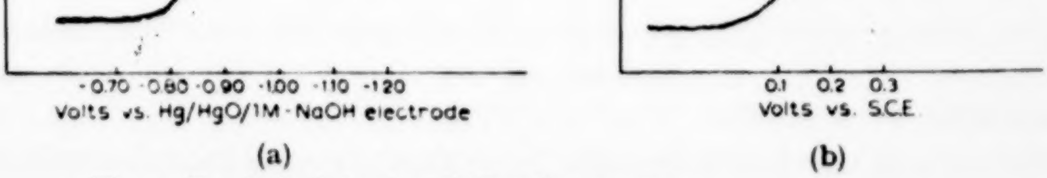


Fig. 1. Dependence of wave height of plutonium reduction wave on concentration of alkali.



(a) (b)

Fig. 2. Typical plutonium(VI) polarograms:
(a) Plutonium(VI) wave in 0.68N NaOH base solution,
(b) Plutonium(VI) wave in 0.18M oxalate base solution.

where E_{de} is the potential of the dropping mercury electrode, i is the corresponding current and i_d is the diffusion current. Plots of E_{de} against $\log \frac{i}{i_d - i}$ interpolated to $\log \frac{i}{i_d - i} = 0$ yielded $E_{1/2}$ values of -0.207 ± 0.002 V against the saturated calomel electrode. Values of n, found from the slopes of the plots varied from 0.90 to 0.99, confirming that the observed reduction is plutonium(VI) to plutonium(V). One such plot is shown in Fig. 3.

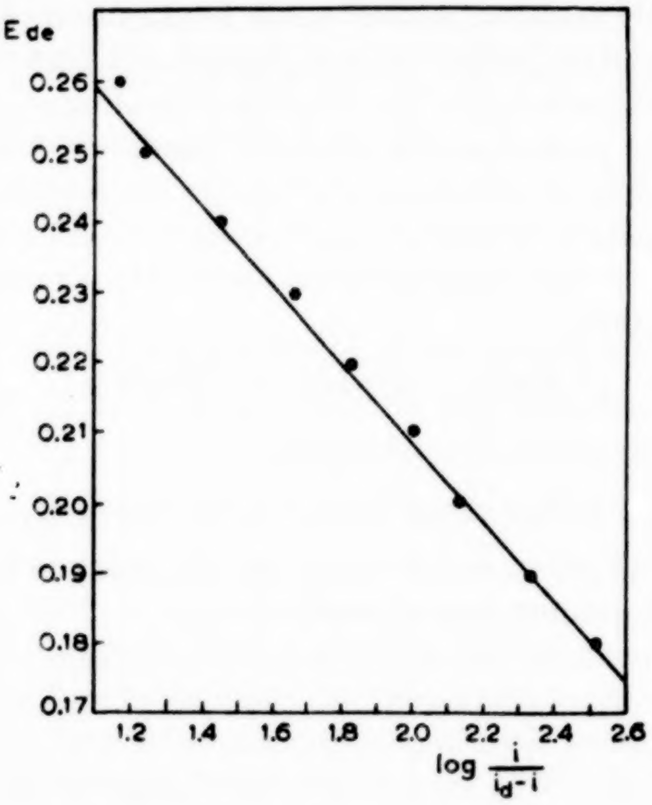


Fig. 3. Plot of E_{de} against $\log \frac{i}{i_d - i}$ for plutonium(VI) reduction wave in oxalate base.

The effect of plutonium(VI) concentration upon the diffusion current for this reduction is shown in Table II.

TABLE II

µg Pu(VI)/ml	4.5	90	180	450	900
i_d (µA)	0.15	0.38	1.1	3.8	9.4

It is apparent that the diffusion current increases at a rate proportional to a power of the plutonium(VI) concentration greater than unity. A logarithmic plot of the data of Table II gives a straight line of slope 1.38. It is thus evident that a secondary process is occurring in addition to the simple reduction of plutonium(VI) to plutonium(V). A similar effect has been observed by KOLTHOFF AND HARRIS[7] with the polarographic reduction of uranium(VI) in hydrochloric acid of concentration 1 M or greater. This behaviour was shown to be consistent with the disproportionation of uranium(V), which is unstable in all but very weak acid solutions. They considered the mechanism to be

$$2\,UO_2^{+} + H^{+} \rightleftharpoons UO_2^{+2} + UO^{+}OH \quad \ldots\ldots\ldots\ldots \quad (1)$$

from which it is clear that enhancement of the uranium(VI) reduction wave due to this disproportionation will increase with increasing uranium concentration.

It is probable that a similar mechanism can account for the results for plutonium, even though the experiments were carried out at a pH ensuring maximum stability of plutonium(V). The large shift in half-wave potential of the plutonium(VI) reduction wave in oxalate solutions from the formal potential of the plutonium(VI)/plutonium (V) couple in essentially non-complexing media implies that plutonium(VI) is much more strongly complexed by oxalate than is plutonium(V), and hence the presence of a large excess of oxalate will induce the disproportionation of plutonium(V) by continuously removing the plutonium(VI) formed. This effect will be enhanced by the strong oxalate complexing of plutonium(IV)[8]. It has been demonstrated by CONNICK[9] that the disproportionation of plutonium(V) cannot be adequately described by a mechanism analogous to that of equation (1) above. He considers the mechanism to comprise the slow reaction:

$$Pu(V) + Pu(III) \rightarrow 2\,Pu(IV) \quad \ldots\ldots\ldots\ldots \quad (2$$

coupled with the rapidly attained equilibrium

$$Pu(V) + Pu(IV) \rightleftharpoons Pu(III) + Pu(VI) \quad \ldots\ldots\ldots\ldots \quad (3)$$

Nevertheless the overall effect is the same and the extent of disproportionation is dependent upon the plutonium concentration.

The induced disproportionation of plutonium(V) in oxalate solution as a result of strong oxalate complexing of plutonium(IV) and plutonium(VI) receives support from spectrophotometric studies. Solutions of plutonium(V) were prepared by the method of GEVANTMAN AND KRAUS[10] at pH 3.5 and the changes in its absorption spectrum within the wavelength region 500–900 mμ were followed on the addition of sodium oxalate-oxalic acid solution up to a fourfold excess over the plutonium. The characteristic pale pink colour of plutonium(V) changes to a light brown colour and a precipitate of plutonium(IV) oxalate slowly forms. The absorption spectrum shows a general intensification together with the characteristic absorption peaks of plutonium(IV) in oxalate solution (550 mμ, 662 mμ, 797 mμ). There are also indications of the plutonium (VI) oxalate peaks at 642 mμ, 787 mμ and 835 mμ, though these are appreciably masked by the intense plutonium(IV) spectrum. The uncomplexed plutonium(V) peaks at 772 mμ and 842 mμ become obscured on addition of oxalate but the peak at 567 mμ, though diminished in intensity, is unshifted. The predominance of plutonium(IV) in the final solution suggests that the disproportionation of plutonium(V) is accompanied by direct reduction of it by oxalate ion.

ACKNOWLEDGEMENT

The authors thank the Managing Director, United Kingdom Atomic Energy Authority (Industrial Group), for permission to publish this paper.

SUMMARY

Polarographic reduction waves at the dropping mercury electrode have been obtained for plutonium(VI) in several complexing media. In oxalate base solution a reversible wave is obtained

corresponding to the reduction of plutonium(VI) to plutonium(V). The non-linear dependence of diffusion current upon plutonium(VI) concentration for this reduction is consistent with the induced disproportionation of plutonium(V) in oxalate solution.

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Received November 4th, 1957

A STUDY OF THE FLAME EMISSION CHARACTERISTICS OF LANTHANUM IN AN AQUEOUS-ALCOHOLIC MEDIUM*

by

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Since a number of the samples which are being analyzed in this laboratory contain lanthanum, it was essential that a relatively simple method be developed to determine this element in a variety of materials, such as thorium oxide, didymium oxide, uranium compounds, and glass. At present, no methods for the direct determination of small concentrations of lanthanum exist, while, for large quantities of the element, several separation steps are required to isolate it from interfering substances. In recent years, advances have been made in the field of flame photometry through the use of improved optical systems, the application of more sensitive detecting devices, such as photomultiplier tubes, and the use of higher flame temperatures. As early as 1934, Lundegardh[1] reported that, in the blue region of the spectrum, at 438 and 442 mμ, the emission of the lanthanum oxide bands offers a sensitive means of determining this element. Piccardi[2] studied the emission of lanthanum in an oxy-hydrogen flame, while Rodden and Plantinga[3] reported the results of a study with a hand spectroscope with a spark-in-flame discharge at 437.2, 441.8, and 560.0 mμ. Recently, Pinta[4] and Ishida[5] investigated the spectrum of lanthanum by means of a spectrograph and a filter-flame photometer. Ishida limited his study to the red and yellow regions of the spectrum.

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* Work carried out under Contract No. W-7504-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Nuclear Company, a division of Union Carbide and Carbon Corporation for the Atomic Energy Commission.

DeAlbinati[6] also reported results of the determination of lanthanum in uranium after removing the latter element through an extraction with ether. He utilized the oxide band which emits at 442 mμ.

The present investigation, which was carried out in the two laboratories, includes a study of the characteristics of all the prominent lanthanum oxide bands with the exception of the one at 590 mμ. In addition, two instruments, one of which has a prism system and the other a grating monochromator, were evaluated. Several photomultiplier tubes, which exhibit maximum response in the region where lanthanum emission bands occur, were tested. The spectra were recorded automatically in order to facilitate the measurement of the peak heights *versus* any background emission and to simplify the collection and interpretation of the data. Various alcoholic media and flame sources, such as oxy-hydrogen and oxy-acetylene, were tested in an effort to improve the characteristics of the lanthanum emission bands. Although it was found that a large number of materials interfere with the flame photometric determination of lanthanum in complex mixtures, these interferences are circumvented by application of a standard addition procedure[7].

EXPERIMENTAL

Apparatus

The instrument utilized in the work conducted at the University of Tennessee was a Beckman Model DU spectrophotometer equipped with a flame attachment, a photomultiplier unit, and a spectral-energy recording attachment, all of which are available from Beckman Instruments, Inc., South Pasadena, California. A 10-mV Bristol recorder with a 2/3-second pen response in conjunction with a wave-length motor drive operating at 0.17 r.p.m. was used to record the emission data.

In the work conducted at the Oak Ridge National Laboratory, an ORNL recording, single-beam flame spectrophotometer, which was developed at the Laboratory, was used. This instrument incorporates a Bausch and Lomb grating monochromator, available from Bausch and Lomb Optical Company, Rochester, N.Y. The optical system of this monochromator contains a grating which has a linear dispersion of 6.6 mμ/mm of slit width. Other principal components of this instrument are a phototube housing for the various photomultiplier tubes; a wave-length drive which operates at the rate of 10 to 200 mμ/min; and a Brown Electronik Recorder, which has a 10-mV range and 2-second pen response. The photomultiplier tubes which were used are Farnsworth 16

Instrument settings	*Beckman DU*	*ORNL Model*
Sensitivity control	7.0 (From clockwise limit)	High
Selector switch, position	0.1	High
Phototube resistor, megohms		
Blue-sensitive	22	5
Red-sensitive	10,000	5
Phototube, V per dynode		
Blue-sensitive	60	70
Red-sensitive	—	80
Acetylene, cm^3/min		
Aqueous medium	1410	—
Alcoholic medium	2000	—
Hydrogen, cm^3/min	—	1050
Oxygen, cm^3/min	3130	3480
Slit, mm, 400–700 mμ	0.050	0.25
700–900 mμ	0.30	0.50

PMI (Farnsworth Company, Fort Wayne, Ind.), RCA-6217, and RCA-1P21, -1P22, and -1P28, available from the Radio Corporation of America, Camden, N.J., A more detailed description of the components of this instrument will be published by KELLEY AND FISHER[8].

The flow of oxygen and fuel through the burner of each instrument was calibrated by means of a wet-test meter.

Reagents

Standard solution of lanthanum, 100 μg/ml. Dissolve 0.117 g of lanthanum oxide, dried at 110°, in 5 ml of 72% perchloric acid. Evaporate the solution to approximately 1 ml; then dilute to 1 l with demineralized water.

Operating conditions

Instrument settings. The instrument settings for both instruments, the ORNL spectrophotometer and the Beckman DU flame spectrophotometer, are given on p. 180.

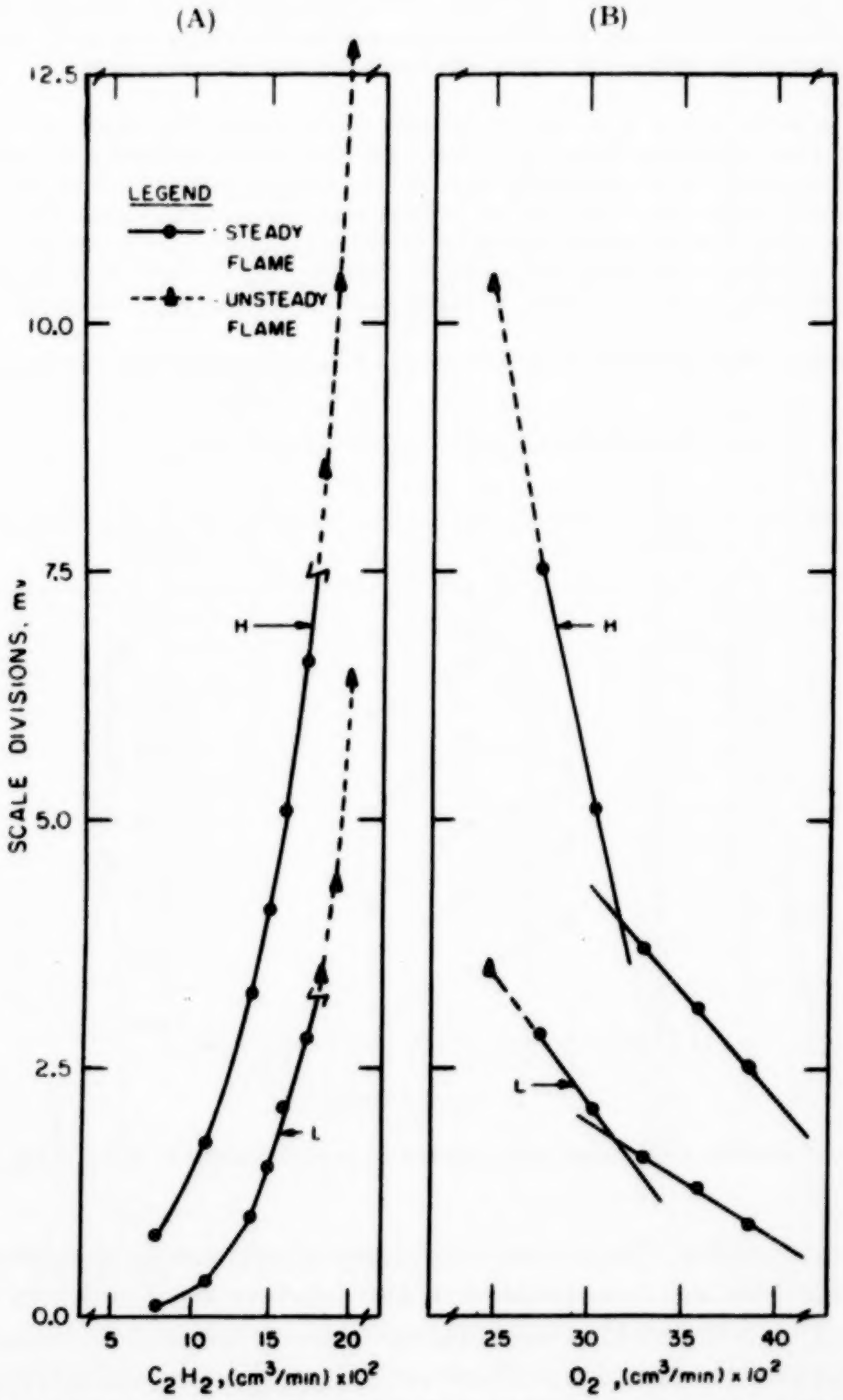

Fig. 1A and 1B. Effects of various flow rates of oxygen and acetylene.

Flow rate of fuel and oxygen. In order to determine optimum conditions at which a maximum, steady flame emission of lanthanum is obtained, the flow rates of oxygen and fuel were established. On investigation, it was found that these optimum conditions are widely variant in aqueous or alcoholic media.

Aqueous solutions. The flow rate of oxygen was maintained at a constant flow of 3100 cm^3/min, while the acetylene was fed into the flame at various rates. In Fig. 1A, a plot is given of the net emission intensity (L) of lanthanum at 560 mμ *versus* the flow rate of acetylene. The background (H), measured at 559 mμ, is also shown in the same figure. From these data, it is evident that the emission intensity of the oxide band and the background radiation increases proportionally as the amount of acetylene entering the flame is increased; however, at a flow rate above 1500 cm^3/min of acetylene, the flame becomes unsteady and reproducible measurements cannot be obtained.

To establish the optimum flow rate of oxygen, acetylene was used at a constant flow rate of 1400 cm^3/min, while the oxygen flow was varied. It was found, Fig. 1B, that the emission intensity of the lanthanum oxide band and the flame background increase as the oxygen flow rate of oxygen is approximately 3200 cm^3/min. This inflection in the emission intensity curves was observed when the ratio of the flow rate of oxygen to acetylene was 2.25. When the ratio of oxygen to acetylene drops below 2.0, unsteady flame conditions are evident.

In alcoholic medium. In a 1 to 1 volume mixture of methanol and water, with an oxygen–hydrogen or an oxygen–acetylene flame, the optimum flow rates for fuel and oxygen differ considerably from those found for aqueous solutions. In Fig. 2, a plot is given of the lanthanum emission for the 743-mμ oxide band, corrected for the background, *versus* the oxygen flow rate for a series of acetylene flow rates. The emission intensity of the lanthanum band increases proportionally as the amount of acetylene entering the flame is increased up to a ratio of oxygen to acetylene equal to approximately 1.6 to 1.7. Only a slight increase in emission intensity is observed for smaller ratios.

In a similar manner, the optimum ratio of hydrogen to oxygen was found to be approximately 2.8.

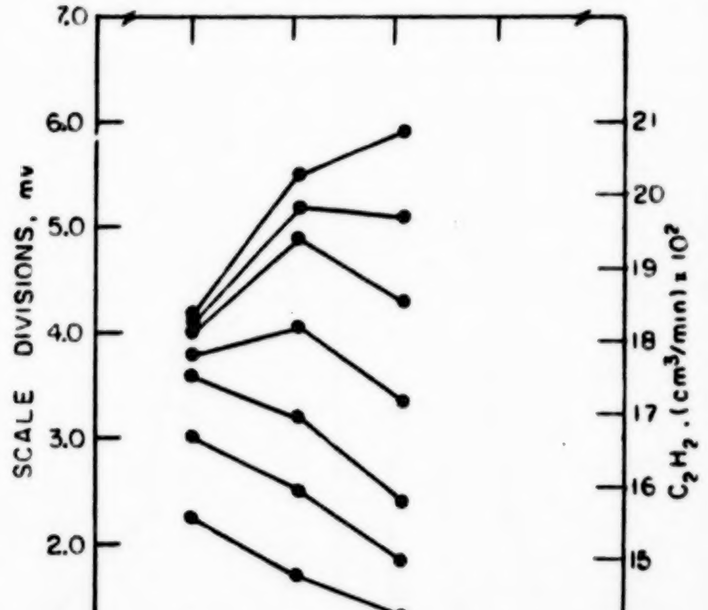

Fig. 2. Effects of various flow rates of oxygen and acetylene for a 50 % methanol solution.

Effect of alcoholic media. The emission intensity of lanthanum is increased markedly when various alcohols are incorporated in the solution aspirated into the flame, as shown in Fig. 3. A solution that contains 90% by volume of methanol produced a large enhancement of the lanthanum flame emission; however, the solvent composition is too critical for the accuracy that is desired, due to the steep slope of the curve. Con-

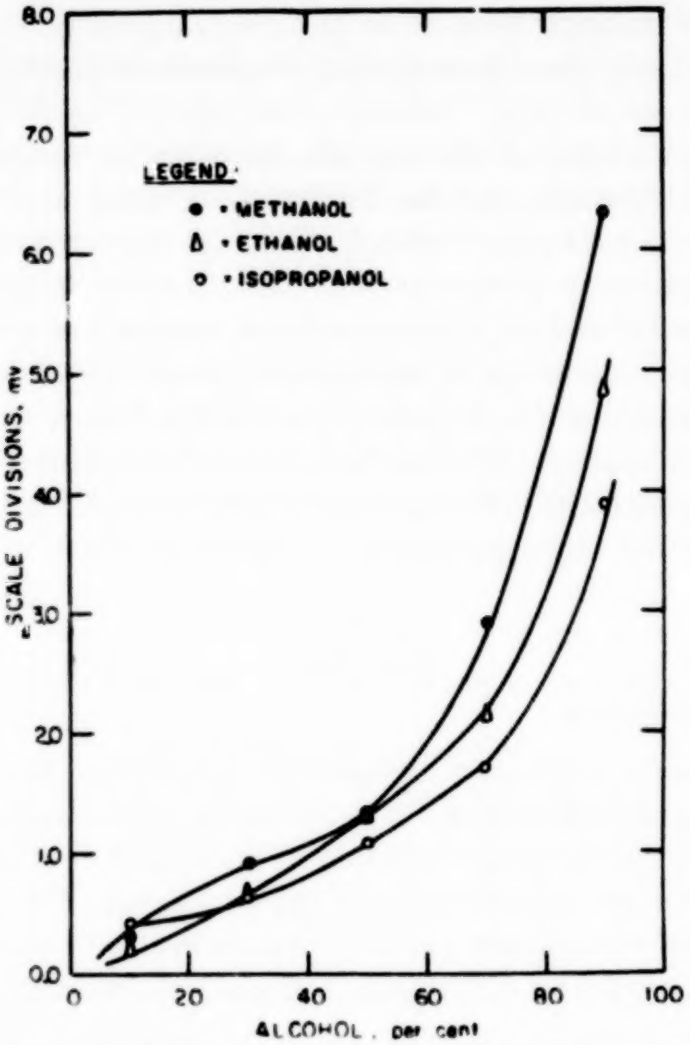

Fig. 3. Effect of the composition of various alcoholic solutions on emission intensity.

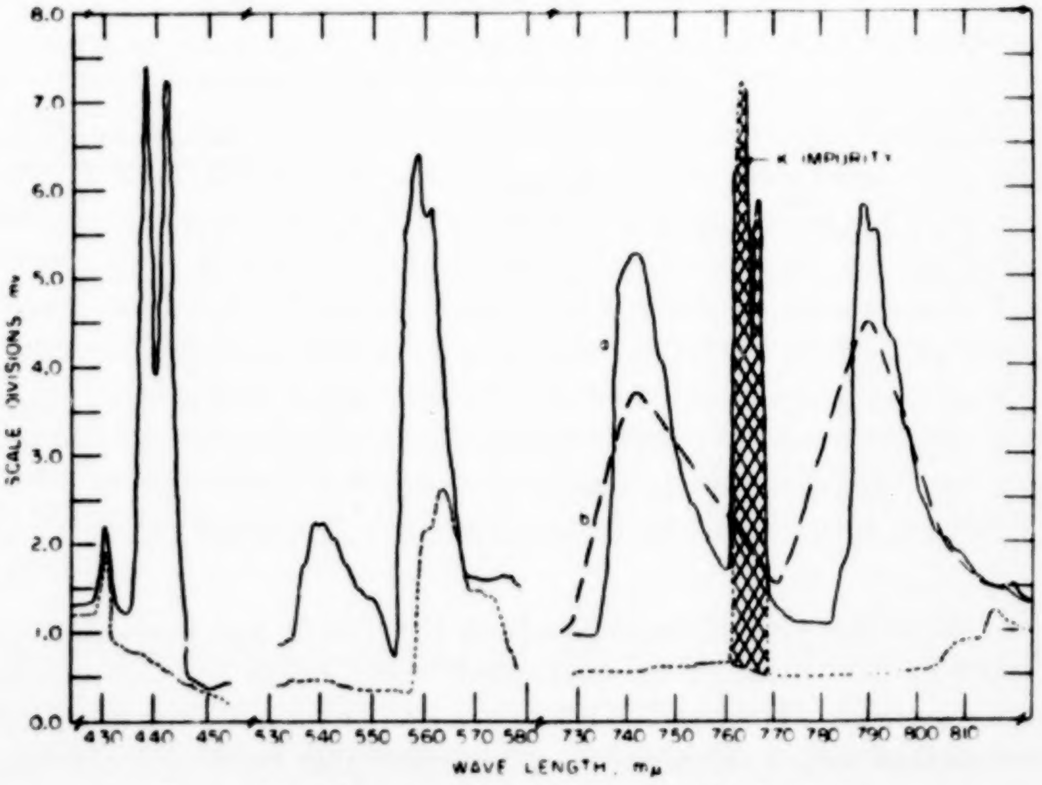

Fig. 4. The flame emission spectrum of lanthanum
a ORNL Model
b Beckman DU
---- Flame background

centrations of alcohol, ranging from 20 to 50% by volume, give flame emissions that lie on the flatter portion of the curve when the emission is plotted *versus* the per cent alcohol.

Using the oxide band head at 560 mμ, the influence of various alcohols upon the flame spectrum of lanthanum and the flame background was also studied. Of the mixtures investigated, methanol-butanol-water in the proportion 30:30:40 gave the largest emission intensity for lanthanum; however, the flame background, correspondingly, is large and unsteady. Unsteady flame backgrounds are also observed for 20 and 50% solutions by volume of isopropanol. A methanol-water solution in the ratio of 1 to 1 is recommended for the most reproducible flame conditions. The emission intensity of lanthanum is increased five-fold in the 50% methanol solution as compared with aqueous solutions and the fluctuations of the flame background are minimized in comparison with other alcoholic media.

DISCUSSION

Flame spectrum of lanthanum

The flame spectrum of lanthanum, which was determined by aspirating a solution that contained 100 μg/ml of lanthanum into the flame, consists of a series of oxide bands that are degraded toward the long wave length in the region of 437 to 445 mμ, 538 to 568 mμ, 587 to 598 mμ, 701 to 772 mμ, and 791 to 860 mμ. The data are presented in Table I and Fig. 4. The wave length and the relative intensity of each of these emission bands are given. A comparison of different red-sensitive photomultiplier tubes is also included in the table.

TABLE I

RELATIVE SENSITIVITY OF THE FLAME EMISSION PEAKS OF LANTHANUM OXIDE IN WATER FOR VARIOUS PHOTOMULTIPLIER TUBES

Wave length, mμ	*Spectral band width mμ*		*Phototube V/stage:*	*Relative sensitivity, μg/ml per scale division*			
				Beckman	*ORNL*		
	Beckman	*ORNL*		*1P28* *60*	*1P28* *95*	*6217* *95*	*16PMI* *90*
437	1.0	1.5		0.7	0.7	0.15	1.5
442	1.0	1.5		0.7	0.6	0.10	1.5
541–43	1.4	1.5		1.4	2.8	0.5	3.2
560–63	1.4	1.5		0.6	0.6	0.08	0.6
590–93	1.6	—		0.8	—	—	—
740–43	16.2	3.3		5.0	—	0.7	0.1
791–94	18.6	3.3		4.5	—	—	0.1

Consideration of the several band heads in the visible and near-red region of the spectrum showed that most of the prominent band heads emit approximately the same emission intensity. The band heads at 740 and 791 mμ are the most sensitive but only in conjunction with a red-sensitive photomultiplier tube. A spectrophotometer, such as a Beckman, Model DU, equipped only with a blue-sensitive photomultiplier tube, can be applied more advantageously to the measurement of the band heads at 438 and 442 mμ, and a series of closely spaced band heads at 560 mμ.

Slit width

The ratio of emission signal-to-flame background is affected by the choice of slit width. The ratio, which is the net band-emission value divided by the background value, should be kept as low as possible. With a filter type of flame photometer, this variable is fixed by the spectral transmission of the particular filter; however, with a monochromator, such as is incorporated in the Beckman flame spectrophotometer and the ORNL grating instrument, the operator can select an optimum ratio for the lanthanum band systems. The results that were obtained for various slit widths of the band head at 437 mμ and the background taken at 435 mμ are tabulated in Table II. On the basis of the results, it is noted that a slit width of 0.050 or 0.060 mm gave the optimum response. A photomultiplier attachment or equivalent amplification of the photocurrent is necessary in order to make it feasible to measure the lanthanum flame emissions at these narrow slit openings.

TABLE II

INFLUENCE OF SLIT WIDTH ON THE RATIO OF EMISSION TO FLAME BACKGROUND

Slit width		*Emission intensity in scale divisions*		
Beckman mm	*Spectral slit, mμ*	*Net band emission, A at 437 mμ*	*Flame background, B at 435 mμ*	*A/B*
0.030	0.98	6.7	35.0	0.191
0.040	1.04	10.0	51.0	0.196
0.050	1.30	14.8	70.7	0.209
0.060	1.56	22.3	112	0.200
0.070	1.82	30.3	162	0.187
0.080	2.08	34.5	210	0.164
0.090	2.34	46.0	280	0.164
0.100	2.60	56.5	362	0.156

Influence of various elements

A major part of the experimental work was concerned with determining the interference, if any, caused by the various cations generally associated with lanthanum. For each substance tested, a series of solutions were prepared which contained several known concentrations of the ion and 100 μg of lanthanum per ml. In Table III the effect of various cations on the determination of lanthanum is presented. The lanthanum band heads at 437, 442, and 560 mμ were investigated principally with an oxy-acetylene flame; while those at 743 and 790 mμ were studied mainly with an oxy-hydrogen flame and a grating photometer equipped with a red-sensitive photomultiplier tube. The latter studies were extended to methanol-water solutions, and were investigated only in the red portion of the spectrum where the emission sensitivity of lanthanum is greatest.

On the basis of these studies the cations can be grouped roughly into these categories:

1. A general interference, consisting of a severe depressant effect, is observed for aluminum, cobalt, copper, chromium, nickel, manganese, titanium, zirconium, and thorium.

2. An increase in background is produced by many of the elements which were tested, such as thorium, uranium and the transition elements, but this effect can be compensat-

ed for by making a separate measurement of the flame background at an appropriate wave length as indicated in the discussion of the flame characteristics of lanthanum.

3. A direct spectral interference is observed with many elements. Sometimes this type of interference can be mitigated by the use of narrow slits, as with potassium, but with a corresponding need for a sensitive photodetector. Enhancement at 437 mμ is significant for more than 100 μg of calcium and iron per ml, and for more than 500 μg per ml of boron. Similarly, calcium, iron and manganese interfere with the band head of lanthanum at 442 mμ because of their own oxide band emissions. The largest number of interferences in this category affect the lanthanum emission at 560 mμ. Chromium, copper, manganese, iron, boron, calcium, barium and the rare earths, erbium, ytterbium, holmium, dysprosium, gadolinium, praeseodymium and yttrium[4] each possess

TABLE III

TOLERANCE LIMITS OF DIVERSE IONS

Concentration of diverse ions in μg/ml necessary to cause results to be 10% low
Samples contain 100 μg of lanthanum per ml
Aq = aqueous, Me = 1:1 water–methanol

	Wave length, mμ						
	437	*442*	*560*	*743*		*790*	
	Aq	*Aq*	*Aq*	*Aq*	*Me*	*Aq*	*Me*
Li	(+)100	(+)100	(+)100	100	500	10	500
Na	(+)100	(+)100	(+)100	10	100	10	100
K	>1000	>1000	100	100	>500	10	100
Rb				100	100	(+)10	(+)10
Cs				500	500	>500	>500
Mg	>500	500	500	>500	>500	>500	>500
Ca	(+)500	(+)500	a	100	>500	100	>500
Ba	>1000	(+)1000	a	100	>500	100	(+)10
Sr	500	100	100				
B	500	500	a	10	100	10	100
Al	5	5	5	10	5	10	5
Y				100	10	100	100
Cr	5	5	a	10	10	10	10
Mn	10	10	a	100	500	100	500
Fe	200	(+)200	>200	100	500	100	>500
Co	10	10	10	100	500	100	100
Ni	100	100	100	100	>500	100	>500
Cu	100	100	100	100	500	100	100
Zn	200	200	200	>500	>500	>500	>500
Cd	>500	500	>500	500	500	500	500
Pb	>500	>500	>500	100	500	100	>500
Ti				100	10	100	10
Zr				100	10	100	10
Ce				(+)100	100	100	(+)100
Th				>500	100	>500	100
U				>500	>500	>500	>500
Pr				100	100	100	100
Nd				100		>500	>500
NH_4	>5000	>5000	>5000				

(+) A positive error; all others are quenching effects.
> Tested quantities of diverse ions that did not produce an effect.
a, Direct spectral interference.

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oxide bands in this region of the spectrum; also, sodium has an emission line at 569 mμ and lithium one at 556 mμ.

4. The alkali metals, especially lithium and potassium, when present in small concentrations (100 μg/ml) produce an enhancing effect in the flame emission of lanthanum. This effect is overcome when larger concentrations of these elements are present (1000 μg/ml). This effect has been referred to as a radiation buffer.

In addition to the correction which can be applied for the background contribution, some interferences can be avoided or mitigated by the proper choice of wave length or solvent. In general, the interferences from a number of elements is lessened or avoided when emission intensities are measured at the higher wave lengths, 743 mμ or 790 mμ. Examples of these are iron, manganese, and copper. At these higher wave lengths the use of alcoholic media, with few exceptions, also increases the tolerance for diverse ions. The two notable exceptions are thorium and zirconium, in that the aqueous medium produces a lesser quenching of the lanthanum emission.

Although a large number of elements interfere with the emission intensity of lanthanum at all the five prominent band heads, the interferences are generally not severe enough to preclude the use of the method of standard addition, as described by CHOW AND THOMPSON[7], for evaluation of the lanthanum content of many types of samples. The validity of this method of evaluation is substantiated by the results shown in Table IV, obtained with samples of didymium oxide, synthetic solutions approximating the composition of certain pH-responsive glasses[9], solutions of thorium (from the oxide), and samples of uranium.

RECOMMENDED PROCEDURE

In the absence of interfering ions

In case where the concentration of foreign ions is below the quantities noted in Table III, a calibration curve may be applied to the estimation of lanthanum. To prepare a calibration curve, aspirate solutions which contain 5 to 100 μg of lanthanum per ml under conditions that are described in the section "Operating conditions" and measure the intensity at the selected wave length. A linear relationship exists between lanthanum concentration and emission intensity over this range, after a correction is made for the background contribution.

In the presence of interfering ions

If diverse elements are present in concentrations which are known to cause interferences, a standard addition method can be applied. For that purpose, equal portions of a solution containing the sample are added to a series of solutions containing the lanthanum standard in varying known concentrations; then the solutions are adjusted to the same final volume. The emission intensity of lanthanum in these solutions is then determined as described previously. These values are plotted on a rectilinear graph *versus* the concentration of the standard. By extrapolating the calibration line until it intersects the ordinate, the value corresponding to the concentration of lanthanum in the unknown sample can be established from the intersection point.

A series of samples including thorium, uranium, synthetic glass and didymium oxide were analyzed by this procedure and the results are presented in Table IV.

Thorium oxide. Weigh a 2.5-g portion of thorium oxide and transfer it to a 250-ml beaker. Add 5 ml of $15N$ HNO_3, 15 ml of 70% $HClO_4$, and two drops of 48% HF. Heat the sample to strong fumes of $HClO_4$ and maintain until the sample is dissolved. After the sample cools, transfer it to a 100-ml volumetric flask and dilute to 100 ml. Transfer three 10-ml aliquots into 25-ml flasks. Carry out the rest of the procedure as described in the previous section. From the representative data in Table IV for synthetic mixtures, it can be noted that 0.1% of lanthanum can be determined within 10%.

Uranyl sulfate solution. Transfer a portion of the solution containing approximately 0.25 g of uranium into a 25-ml volumetric flask and dilute to the calibrated volume with water. Follow the steps described in the standard addition procedure. The results from known mixtures are presented in Table IV.

Glass. A synthetic sample was prepared of a glass used in the manufacture of pH glass electrodes that have a low sodium error[9], after which the lanthanum content was determined. The composite solution of glass was prepared to contain the following weight per cent of oxides: SiO_2, 54.5; La_2O_3, 14.7; BaO, 11.0; CaO, 1.6; Cs_2O, 12.5; and Li_2O, 10.8 in a 100-ml volume. A 10-ml aliquot of this mixture was diluted to 100 ml and used for the evaluation of its lanthanum content by a method of standard addition. The values found by measuring the emission of lanthanum oxide at several wave lengths are presented in Table IV. It is notable that evaluation of lanthanum oxide is feasible at 560 mμ even though the BaO band partially overlaps the background measurements at 559 mμ. The effect due to the presence of barium in the sample was compensated for in this case by having a constant amount of barium present in solutions carried through the standard addition procedure.

TABLE IV

DETERMINATION OF LANTHANUM IN VARIOUS MATERIALS

Material	*Lanthanum oxide*					
	% present	*% found at wave length, mμ*				
		437	*442*	*560*	*743*	*790*
Thorium	0.12				0.11	0.11
					0.11	0.12
Uranium	0.23				0.21	0.22
					0.23	0.22
	0.47				0.48	0.45
Synthetic glass	14.7		15.4	14.6		15.9
			16.0	13.8		
				14.6		
Didymium oxide	44	41.1	39.9	39.3	39.3	
		40.5	38.1	39.3	39.3	
		39.9	38.1	39.3	39.3	

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Didymium oxide. A sample of didymium oxide (Code No. 420) which was received from Lindsay Chemical Company, Chicago, Ill., was reported to have the following percentage composition: La_2O_3, 44; CeO_2, 1; Pr_6O_{11}, 9.5; Nd_2O_3, 32; Sm_2O_3, 5.5; Gd_2O_3, approx. 3; Y_2O_3, approx. 3; others, approximately 2. A 1-g sample was weighed and transferred to a 250-ml beaker; then 15 ml of 70% $HClO_4$ was added. The contents were boiled until the sample dissolved. After dissolution of the sample, it was cooled and transferred into a 100-ml volumetric flask and diluted with water to the calibrated volume. From this solution, four 1-ml aliquots were transferred to a 50-ml volumetric flask and carried through the standard addition procedure. The results of these analyses are presented in Table IV. The values reported in Table IV are approximately 4% lower than the estimate received with the sample; however, the latter value is based on the determination of other constituents and reporting the lanthanum content by difference from 100%.

SUMMARY

The determination of lanthanum by measuring its flame emission at several wave lengths has been evaluated by means of two recording spectrophotometers equipped with special photomultiplier detecting devices. In addition, a comparison of the effect of an aqueous and alcoholic medium was carried out. In general, the interference from foreign ions is least at the higher wave length of 743 mμ. In most cases, especially with transition elements, the interference is lessened when 1:1 water–methanol solution is used. The exceptions to this rule are titanium, thorium, and zirconium which cause less interference in an aqueous solution. The method used in conjunction with a standard addition technique, has been applied to the determination of lanthanum in solutions of thorium oxide, uranium, glass, and didymium oxide mixtures.

ACKNOWLEDGEMENT

The authors acknowledge the assistance of M. A. MARLER in the preparation of this manuscript.

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Received November 25th 1957

THE POLAROGRAPHIC DETERMINATION OF INDIUM IN ZINC-BASE ALLOYS

IV. THE DETERMINATION OF INDIUM IN MAZAK ALLOYS

by

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INTRODUCTION

In previous papers in this series, the development of a general method for the determination of indium in zinc-base alloys, involving the use of the linear-sweep cathode polarograph was described[1] and methods for the determination of this element in "aluminium-free"[2] and "lead-free"[3] zinc alloys have been presented. The first of these requires special instrumentation, not yet generally available, while the other two are not applicable to mazak alloys (aluminium about 4%; lead up to 50 p.p.m.) in which it was desired to determine indium down to a concentration of 0.0001% (1 p.p.m.). This paper described the development of a method applicable to mazak alloys which may be carried out by conventional polarography.

In the course of the work already reported, the use of a "collection" procedure for selective removal of indium from cadmium, employing zinc oxide, was described[2]. This provided a rapid separation of indium from all interfering elements usually found in zinc alloys, with the exception of aluminium. This element was precipitated at the pH of the "collection" (4.95) and its gelatinous nature made filtration tedious. Significant amounts of other impurities were also co-precipitated. This method was therefore confined to those zinc alloys of negligible aluminium content. No other feasible method of separating indium could, however, be found and it was therefore decided to re-examine the "collection" procedure to ascertain if it could be modified so that the precipitated aluminium could be used as the collector. It was also necessary to overcome the considerable difficulties caused by co-precipitation of interfering elements. In order to check the efficiency of separations easily and quickly, radio-chemical techniques were used for the initial work as described in a previous paper[2]. As before, radio-active indium was used, the isotope being ^{114}In of half-life 49 days.

EXPERIMENTAL AND DISCUSSION

A mazak alloy, of approximately the composition given in Part I of this series[1], was used in this work. Polarography was carried out, as previously, on three types of conventional polarograph[2] at 25° and *versus* the mercury pool anode. All potentials are quoted on the European sign convention. On this convention the potential of saturated calomel electrode (S.C.E.) has been taken as +0.246 V *versus* the normal hydrogen electrode (N.H.E.).

The following experimental procedure was adopted: 10 g portions of the mazak alloy were dissolved in hydrochloric acid, final dissolution being assisted by the addition of hydrogen peroxide. The solutions were then doped with varying amounts of radio-active, or non active, indium. $2M$ sodium hydroxide was then added until the pH, as measured in a Cambridge pH meter, was 4.95 ± 0.1. This precipitated the aluminium and indium hydroxides together as a gelatinous mass. The precipitate was centrifuged and washed with water, the supernatant liquor being removed after each separation. The precipitate was then dissolved in hydrochloric acid and counted, or polarographed according to the nature of the indium added.

Experiments using radio-active indium showed that more than 95% of added indium was recovered. Polarography of the solutions showed that the aluminium hydroxide was heavily contaminated with adsorbed metal ions, mainly copper and cadmium. The amount of copper was usually so large that it prevented the use of the polarograph on maximum sensitivity. The use of this sensitivity was necessary if the required lower limit of detection (1 p.p.m.) of indium was to be attained.

It was not found to be possible to remove the copper and cadmium contamination by further washing of the precipitate, but a study of the standard potentials of the various ion species of copper indicated that copper metal will only dissolve in hydrochloric acid if oxidation also takes place. It was therefore decided to dispense with the final oxidation stage in the dissolution of the alloy and to rely on the hydrogen evolved to displace the oxygen from the solution. Experiments showed that under these conditions only negligible amounts of copper were dissolved and that it was possible to warm the solution for 15 min after effervescence had ceased without significantly increasing its copper content. It was also found, however, that about 8.5% of added indium remained out of solution with the metallic copper.

The problem of cadmium contamination was overcome by redissolving and reprecipitating the aluminium and indium hydroxides, followed by washing and finally dissolving in hydrochloric acid. It was shown with radio-indium that about 0.5% of indium was lost in each precipitation and about 3% in each washing. Two precipitations and washings therefore gave an overall recovery of 85% of the added indium, which was, in the final solution, free from cadmium and almost free from copper.

A standardised procedure was therefore adopted consisting of a double precipitation and washing of the hydroxides. It was found beneficial to add hydroxylamine hydrochloride in the final stages of the determination to reduce any iron present to the ferrous state, thus preventing an interfering step in the region of 0 V applied potential.

Recoveries of added indium from solutions of mazak alloy under these conditions were satisfactory in the range 0.5 to 20 p.p.m. and gave a straight line calibration. Full details of the method are given below.

METHOD

Place two 10-g portions of the mazak alloy sample (as turnings or drillings) in two 400-ml beakers, A and B. Add 1.0 ml of the standard indium solution (Note 1) to beaker B and treat both beakers as follows. Add 45 ml $10N$ hydrochloric acid and warm until effervescence ceases. Allow to stand for 15 min and filter through a No. 41 Whatman filter paper, collecting the solution in a 400-ml beaker. Wash the original beaker and filter paper and add the washings to the filtrate. Discard the residue. Evaporate to 20 ml to remove excess hydrochloric acid and dilute to 50 ml with water. Insert the electrodes of a pH meter and add $2N$ sodium hydroxyde slowly (Note 2) until the pH is

4.95 ± 0.1. Withdraw the electrode and rinse down, letting the rinsings go into beaker. Stir the solution for 10 min.

Divide the solution equally between two balanced 50-ml centrifuge tubes (do not wash out the beaker at this stage). Centrifuge for 5 min, pour off and reject the supernatant liquor. Rinse the beaker with 10 ml water and add it to one of the centrifuge tubes. Add 2 ml saturated potassium chloride and stir for 5 min. Repeat this procedure with the second centrifuge tube using a second 10-ml rinsing of the beaker.

Centrifuge the tubes for 5 min. Pour off and reject the supernatant liquor.

Add 15 ml 10*N* hydrochloric acid to one of the centrifuge tubes and stir with a glass rod until the precipitate is completely dissolved. Pour the solution into the second tube and dissolve the precipitate in this also. Pour the solution into a 400-ml beaker, rinse out both tubes with water and add the rinsings to the beaker. Evaporate the solution to 5 ml.

Add 45 ml 10*N* hydrochloric acid and repeat the filtration, pH adjustment and precipitation, centrifuging, washing and re-dissolution procedures exactly as already described. Again evaporate the final solution to 5 ml. Transfer the solution to a 10-ml calibrated flask, rinse the beaker with small volumes of water and add these to the flask also. Add 0.5 ml 20% hydroxylamine hydrochloride and make up to the mark with water. Immerse the flask in a beaker of water at 60° for 10 min. Cool.

Transfer aliquots of solutions A and B to polarographic cells. Deoxygenate by bubbling hydrogen or nitrogen through them for 10 min and record polarograms over the range —0.45 to —0.75 V on "quarter voltage", (Note 3), using the mercury pool as anode. Measure the step height, D_1, obtained with solution A and, D_2, obtained with solution B. The half-wave potential of these steps is —0.605V. These steps should be recorded on the same polarograph sensitivity setting, or alternatively, the measured step heights should be adjusted to that which would be obtained at a common sensitivity value.

Calculate the indium content of the sample from the expression

$$\text{p.p.m. indium} = \frac{4\,D_1}{D_2 - D_1}$$

Notes

1. The standard indium solution is prepared as follows. Dissolve 0.0121 g pure indium oxide, or 0.010 g pure indium metal in 5 ml 10*N* hydrochloric acid. Transfer the solution to a 250-ml calibrated flask and make up to volume with water.
2. A massive gelatinous precipitate is formed at this stage. Great care must be taken to obtain thorough mixing after each addition of the sodium hydroxide, otherwise an inaccurate pH value will be obtained.
3. "Quarter voltage" refers to a setting of the polarograph such that only one quarter of the normal potential difference is applied to the polarizing potentiometer. This has the effect of "stretching out" the polarogram over the record, making it more easily measurable.

TESTS OF THE METHOD

Determinations were carried out by the method given above, using solutions of mazak alloy, to which known amounts of indium had been added. The recoveries obtained are given in Table I below.

TABLE I

Sample		*Indium (p.p.m.)* *added*	*found*
Mazak	1.	0.4	0.33
	2.	1.0	1.05
	3.	2.0	2.0
	4.	4.0	4.2
	5.	6.0	5.4
	6.	8.0	7.7
	7.	20.0	19.6

A typical polarogram obtained in these determinations is shown in Fig. 1.

In addition to the recoveries listed in Table I, determinations of indium were also made on mazak alloys to which known amounts of indium had been added during manufacture. The results obtained are listed in Table II and are compared with results obtained by emission spectroscopy after the alloy had been converted to oxide.

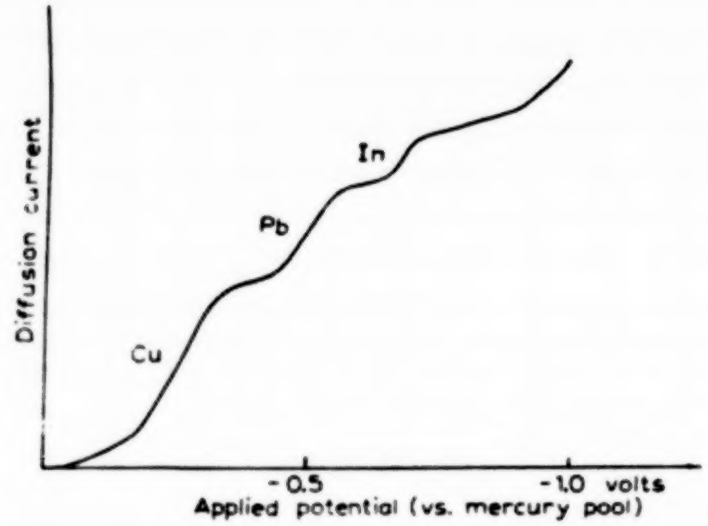

Fig. 1. Copper, lead and indium after "collection" of indium from mazak-type alloy.

TABLE II

Sample	*Nominal indium content p.p.m.*	*Indium found (p.p.m.)*	
		polarographically	*spectrographically*
Mazak A	5	4.0	4.8
B	10	9.0	9.9
M	2	1.6	1.9
W	10	5.7	6.5

It should be noted that in the results presented in Table II, deviations from the nominal values for indium are shown, in close agreement, by both methods. It therefore appears probable that some of the comparatively volatile indium has been lost in the alloying and moulding processes.

The indium steps, as shown in Fig. 1, were of good shape and corresponded to a 3 electron reversible reduction. This must be due to the high chloride concentration of the base electrolyte.

CONCLUSIONS

As a result of the work described in this and in previous papers in this series[1,2,3], four methods for the determination of indium in zinc alloys have been developed. They are as follows:

1. A rapid method employing the derivative circuit of the linear-sweep cathode-ray

polarograph, which is applicable to most zinc alloys provided that the cadmium : indium ratio does not exceed 10:1. If this ratio is exceeded then the indium concentration may be reported as less than $^1/_{10}$th of the cadmium content.
2. A "collection" method applicable to zinc and to zinc alloys provided that their aluminium content is less than 0.01%.
3. A method using an iodide base electrolyte which will determine indium in zinc or in zinc alloys in which lead is absent, or is less than $^1/_{20}$th of the indium concentration.
4. A co-precipitation method which is applicable to almost all zinc alloys, but which is much more lengthy than those mentioned above.

For routine work, the cathode-ray method is the best and this could easily be extended to give determinations of copper, lead and cadmium in the same solution.

SUMMARY

In this paper, the development of a co-precipitation method for the separation of indium from zinc alloys is described and a method for the determination of indium down to 0.5 p.p.m. in mazak alloys is presented. Results obtained in trials of this method are given and the final conclusions regarding this and previously developed methods are included.

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Received November 5th, 1957

THE POLAROGRAPHIC DETERMINATION OF ALUMINIUM*

IV. A STUDY OF THE REDUCTION OF SOME HYDROXYAZO DYES IN RELATION TO THE ALUMINIUM-SOLOCHROME VIOLET R.S. COMPLEX

by

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INTRODUCTION

In previous papers[1] in this series, the methods available for the determination of trace quantities of aluminium have been briefly reviewed and a study of the use of the azo dye Solochrome Violet R.S. has been made. The development of a method for the determination of microgram amounts of aluminium in beryllium has been described and studies yielding some information regarding the structures of the aluminium dye complexes have been reported[1].

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The fundamental work on the aluminium Solochrome Violet R.S. reaction, already reported[2], has established that two complexes exist within the pH ranges 4.25–5 and 5.75–7, having dye–aluminium ratios of 2:1 and 3:1 respectively. The probable mode of reduction of the dye at the dropping mercury electrode was suggested and supported by determinations of electron transfer on reduction, both in the free state and when complexed with aluminium. This work has, however, given no precise information regarding the position of the linkages in, or the configuration of, the complexes.

Complexes of metals with azo dyes have been extensively studied by other workers, but those with aluminium have received little fundamental treatment. The work already carried out by us indicated that the aluminium–dye bonding could not be entirely explained by analogy with the behaviour of other metals and further investigation was therefore undertaken. This report describes some preliminary experiments carried out with azo dyes which differ from Solochrome Violet R.S. in the position and number of their constituent and substituent groups. The results are considered in the light of steric effects and referred to the reported structures of other metal–azo dye complexes.

EXPERIMENTAL

The polarographic reduction of three azo dyes, in the presence and absence of aluminium, was studied in order to provide comparisons with that of Solochrome Violet R.S. The dyes used were Orange II, Resorcin Yellow and Acid Alizarin Black SN. Unless otherwise stated, all polarography was carried out on a Cambridge direct writing polarograph at 25° and *versus* the mercury pool anode. All potentials are expressed in the European sign convention; by this convention the potential of the saturated calomel electrode (S.C.E.) has been taken as +0.246 V *versus* the normal hydrogen electrode (N.H.E.).

Polarography of Orange II

20 ml of 0.05% aqueous solution of Orange II (sodium salt of *p*-sulphobenzeneazo-*β*-naphthol, Colour Index No. 151) were buffered to pH 4.6 with a perchloric acid–ammonium acetate mixture and made up to 50 ml with water. An aliquot of this solution was deoxygenated and polarographed.

A similar solution was also prepared as above, but containing 100 μg of aluminium in addition to the dye. After heating this solution at 70° for 10 min in a water bath an aliquot was deoxygenated and polarographed.

The above two experiments were repeated at pH values 2.0 and 7.05.

In no case was modification of the dye step by aluminium observed. A maximum occurred on all steps but no attempt was made to suppress this. A typical step is shown in Fig. 1. The half-wave potential of the dye step was about —0.61 V *versus* the mercury pool in the case of the solution of pH 4.6.

Polarography of Resorcin Yellow

A sample of Resorcin Yellow was prepared by diazotizing sulphanilic acid and coupling with resorcinol. Two 20-ml aliquots of a 0.05% solution of this dye were placed in 50-ml graduated flasks and 100 μg of aluminium was added to one of them. After adjustment of the pH to 4.6 as described above, the flasks were made up to volume and heated at 70° for 10 min in a water bath. Aliquots from each were then deoxygenated and polarographed.

This experiment was repeated at pH 8.5.

No modification of the dye step by aluminium occurred. A maximum was observed in each case. The half-wave potential of the dye step at pH 4.6 was —0.47 V *versus* the mercury pool. Well-defined steps, without maxima, were obtained on the linear-sweep cathode ray polarograph[3,4].

Polarography of Acid Alizarin Black SN

Ten ml of a 0.05% solution of Acid Alizarin Black SN (disodium salt of 4-sulpho-1-hydroxybenzene-2,5-diazo-*β*-naphthol-naphthol-6-sulphonic acid, Colour Index No. 337) was buffered at pH 4.6 as before and diluted to 50 ml with water. An aliquot was deoxygenated and polarographed.

Initial attempts to polarograph the solution were unsuccessful because the drops of mercury falling from the cathode did not coalesce with the pool anode. A silver–silver chloride anode was therefore substituted. This electrode was prepared as described elsewhere[5]. A composite wave consisting of two incompletely separated steps was then obtained. This solution was also polarographed on the linear-sweep cathode-ray polarograph and the two incompletely separated peaks obtained are shown in Fig. 2A. In order to separate these peaks, the instrument was set for derivative working when two well-defined peaks were obtained. The solution was then heated at 70° for 5 min, cooled and a further aliquot polarographed. It was found that both peaks were shifted to more negative potentials and increased in height without significant alteration in shape (Fig. 2B).

A solution, exactly similar to that described above, but containing 4 μg of aluminium per ml was then prepared, adjusted to pH 4.6 ± 0.1 and polarographed without heating at 70°. Three steps were obtained with approximate half-wave potentials of —0.43, —0.50 and —0.75 V *versus* the silver–silver chloride electrode respectively. The second and third steps suffered mutual interference too seriously for accurate measurement of step height. The solution was then heated at 70° for 5 min, and a further aliquot was polarographed. The separation of steps was much improved and this was further increased by the use of an extended voltage scale[6] as shown in Fig. 3. The half-wave potentials were —0.44, —0.615 and —0.83 V *versus* the silver–silver chloride anode respectively. A very small wave preceded these steps. Polarography was repeated on the cathode-ray polarograph set for normal working, when good peaks were obtained at potentials of —0.54, —0.67 and —0.89 V respectively.

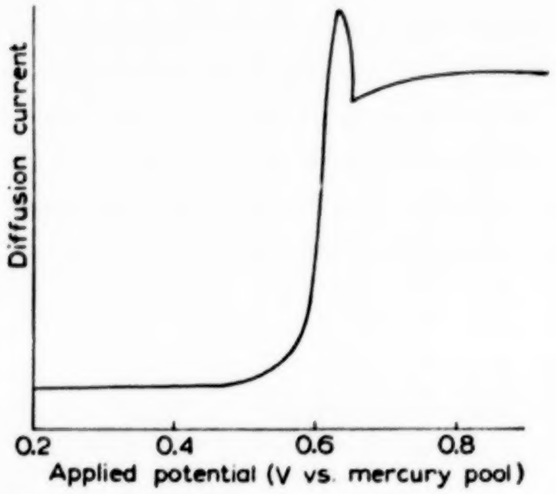

Fig. 1. Orange II. 0.02% at pH 4.6.

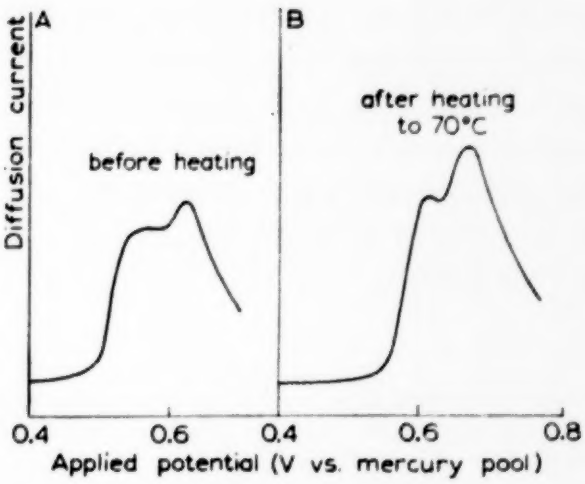

Fig. 2. Acid Alizarin Black SN (0.01% at pH 4.6) cathode-ray polarograph.

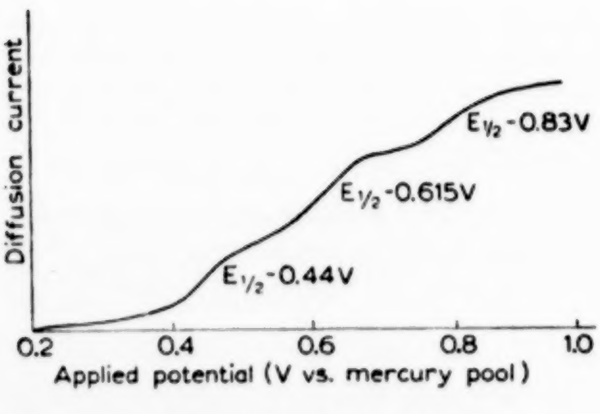

Fig. 3. Acid Alizarin Black SN in presence of 4 μg aluminium per ml at pH 4.6 after heating to 70°.

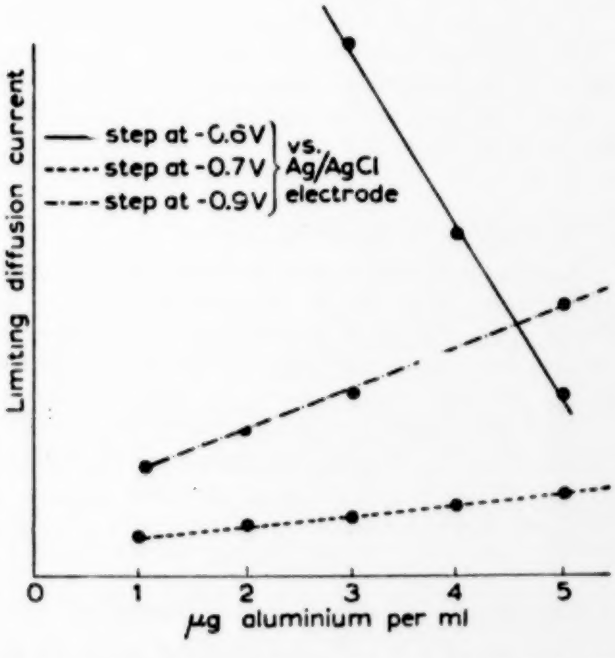

Fig. 4. Step heights due to reduction of Acid Alizarin Black SN (0.01%) *versus* aluminium concentration.

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A series of solutions containing both Acid Alizarin Black SN and aluminium was next prepared, adjusted to pH 4.6 and heated as described above. The concentration of aluminium ranged from 1–5 μg/ml. Except in the case of solutions containing less than 2 μg of aluminium per ml, three measureable steps were obtained and it was found that as the aluminium concentration increased, the first step decreased in height while the heights of the second and third steps increased. Polarography was repeated on the cathode-ray polarograph in view of the greater resolution of this instrument, and the results given in Table I were obtained. The changes of step height are shown in the composite graph in Fig. 4.

TABLE I

Aluminium concentration μg/ml	*1st step*		*2nd step*		*3rd step*	
	Peak height[a]	$E_{1/2}$[b] *V*	*Peak height*[a]	$E_{1/2}$[b] *V*	*Peak height*[a]	$E_{1/2}$[b] *V*
1	460	—0.66	10	—0.79	29.5	—0.99
2	240	—0.60	12.5	—0.71	40	—0.92
3	140	—0.56	15	—0.68	47	—0.91
4	95	—0.56	18	—0.69	39	—0.92
5	50	—0.59	22	—0.70	75	—0.94

[a] These values are in arbitrary units corrected to a single sensitivity setting ($1 \cdot 10^4$) on the cathode-ray polarograph.

[b] These half-wave potentials have been obtained by subtracting 0.05 V from the peak potentials recorded on cathode-ray polarograph[4]. They are quoted *versus* the silver–silver chloride electrode.

Finally, solutions containing 4 μg of aluminium per ml and 0.02% of the dye, having final pH values of 0.7, 6.4 and 10.7 respectively were prepared and polarographed as described above. The first solution yielded a polarogram of half-wave potential about 0.2 V, but consisting of several interfering steps. The second (pH 6.4) gave 4 steps of half-wave potential —0.47, —0.61, —0.72 and —0.99 V respectively. The solution at pH 0.7 gave a well-defined step at —0.68 V, followed by at least two mutually interfering waves at more negative potentials. The three polarograms are reproduced in Fig. 5.

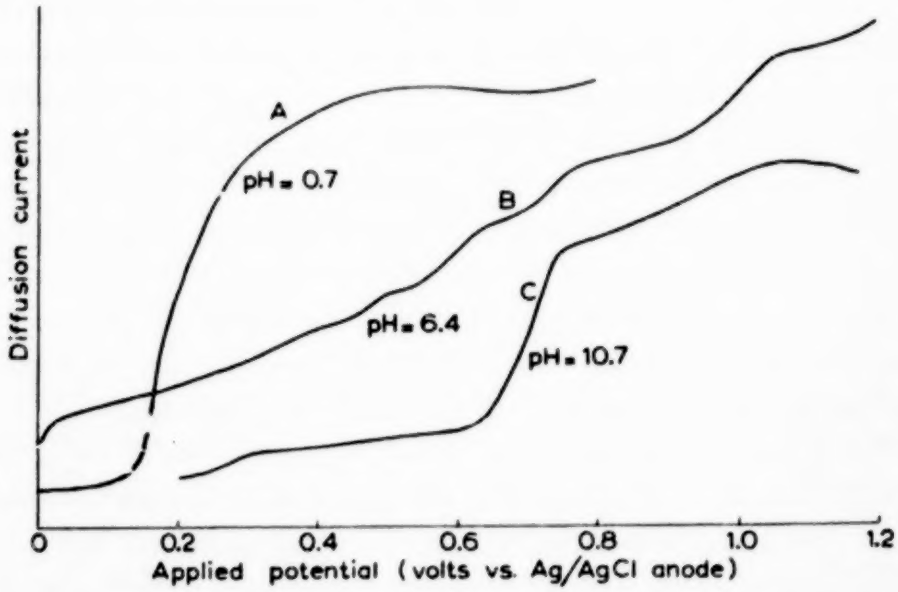

Fig. 5. Polarographic waves of Acid Alizarin Black SN at various pH values.

DISCUSSION

The *cis-trans* isomerism of the parent substance of this group of dyes, azobenzene, has been studied by a number of workers. WINKEL AND SIEBERT[7] found that polarographic reduction of azobenzene and some similar compounds gave a very small step, usually preceding the main step. They suggested that this was due to the existence of *cis-trans* isomers with the equilibrium between them heavily biased. The same suggestion was also made on other grounds by HARTLEY[8], who considered that the *trans* form was the more stable. He was able to prepare the *cis* form by irradiating azobenzene with ultra-violet light. WINKEL AND SIEBERT found that this treatment increased the size of the first step at the expense of the second, which sometimes disappeared altogether. Thermal rearrangement took place on standing.

The relative stability of aryl azo compounds has also been discussed by PAULING[9], who showed that, from consideration of interatomic distances and bond angles in the molecule, the *trans* form was coplanar, but that, in the case of the *cis* form, steric hindrance of the *ortho*-hydrogen atoms prevented such a configuration. X-ray measurements showed that the *cis* form was always rotated 50° out of a coplanar configuration. Since coplanarity is an essential attribute of double bond character, it was assumed that the configuration energy of the *cis* form is small (2–3 kcal) compared with that of the *trans* form. The configuration energy was determined by HARTLEY[8] as 12 kcal/mole and by CORRUCINI AND GILBERT[10] as 10 kcal/mole. BERGMAN, ENGEL AND SANDER[11] present dipole moment data which support these conclusions and it has also been pointed out that when an *ortho*-hydroxy group is present, additional *trans* stability is provided by hydrogen bonding[12].

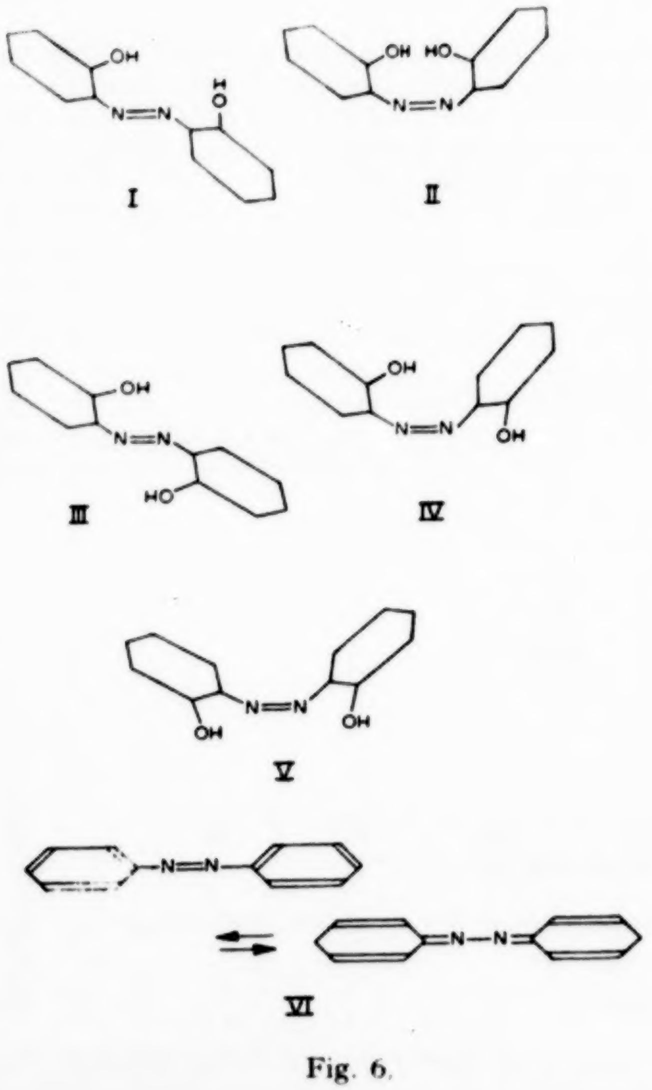

Fig. 6.

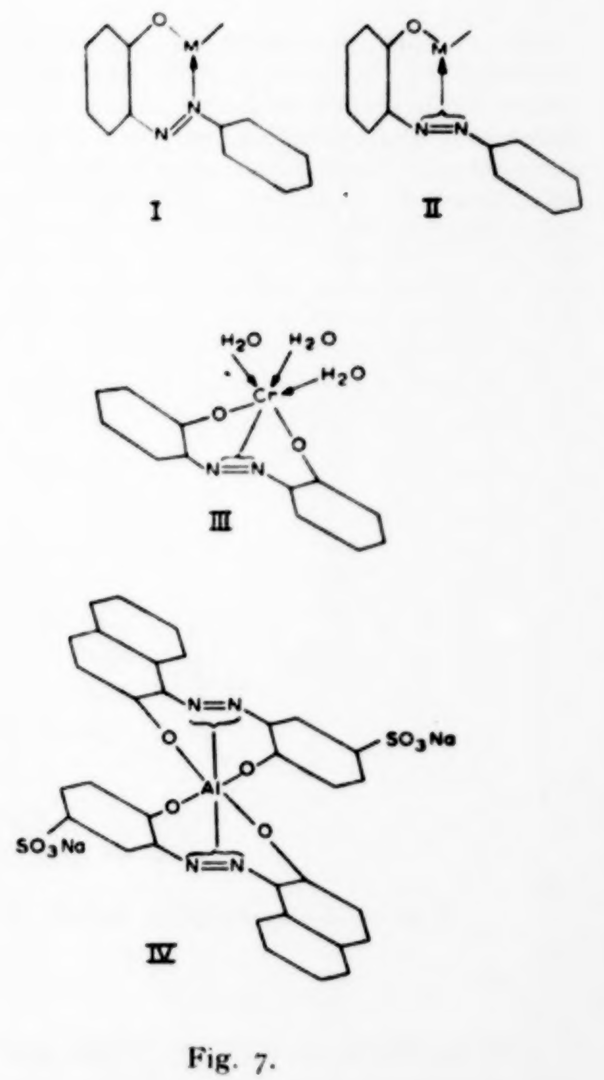

Fig. 7.

In the case of di*ortho*-substituted azobenzenes, five isomers are structurally possible. These are shown in Fig. 6 (I–V). As already stated, the equilibrium in the case of azobenzene is such that the compound is almost completely *trans*. It is to be expected that the tendency will be even greater in the case of the *ortho*-substituted compounds, since steric hindrance will be greater, due to the presence of the larger *ortho*-groups. Structures II, IV and V cannot therefore approach a planar configuration, the distortion being greatest in the case of II and least in the case of V. Although structures I and III and II, IV and V illustrate extreme positions an equilibrium position of the hydroxyl groups must exist. Movement from the equilibrium position by rotation of the rings about the N–C bonds is unlikely to be free. This is due to the existence of resonance between two systems as illustrated in Fig. 6 (VI). The N–C bonds must therefore have some double bond character and the N–N bond some single bond character with consequent restriction of rotation. This is supported by measurement of the bond lengths between these atoms which are found to be less than normal[13].

WILLARD AND DEAN[14] suggest that the reduction in height of the Solochrome Violet R.S. step and the simultaneous appearance of a second step at a point 0.2 V more negative which occurs when aluminium is added, might be caused by the stabilisation of one of the two possible aryl group configurations about the azo group by chelation. We consider that this chelate formation must take place during the heating of the solution at 70°, but transformation of the dye molecule from the *trans* form to the *cis* form, for reasons already discussed, appears improbable.

A number of investigations of the chelate complexes of several metals with dyes of this type have been reported. ELKINS AND HUNTER[15] have presented evidence of chelation in the case of cobalt and nickel with azo dyes having one *ortho*-substituent. They were in no doubt that the stereochemical arrangements of the aryl groups about the azo group is *trans* and proposed a structure in which metal ions form part of a 6-membered ring (Fig. 7 (I)). The existence of this 6-membered ring structure was also specially mentioned by HAENDLER AND SMITH[16].

The azo dye complexes of copper have been extensively studied. DREW AND LANDQUIST[17] have made it clear that they are true Werner complexes and have shown that chelation occurs only when an *ortho*-substituted group is present. *Meta*- and *para*-substitutes have no effect. These authors determined the copper : dye ratio as 1:2 (co-ordination number 4) and stated that the presence of a second *ortho*-substituent would lead to further stability due to fused ring formation.

The metal-azo group bond is now believed to be in resonance between the nitrogen atoms rather than to one of them specially. The azo group therefore occupies one co-ordination position as shown in Fig. 7 (II). The chelate ring is therefore regarded as 5-membered. This is considered to be the most stable chelate structure.

The *ortho*-substituted azo dye complexes of a number of metals have been studied by CALLIS, NIELSEN and BAILAR[18]. These authors have reviewed the earlier work and have reported a 3:1 dye to metal ratio in the case of complexes formed between cobalt and a mono-substituted azo dye. They considered that fused-ring systems are formed with di*ortho*-substituted dyes and that complexes with dyes of this type are more readily formed and more stable. They assigned a fused ring structure to the trivalent chromium complex as shown in Fig. 7 (III). Similar structures for the vanadium complexes were reported by SWENAGA[19].

From the above considerations and from the results of our work we conclude that aluminium forms a true Werner complex with an *ortho*-hydroxy-azo dye by replacement of the hydrogen atom of the hydroxy group or groups, and the acceptance of an electron pair from the nitrogen atoms in resonance. It is also accepted that the configuration of the dye molecules in the complex is *trans*.

The failure to obtain a shift of half-wave potential with Orange II which contains only one *ortho*-hydroxy group indicates that aluminium does not chelate into a simple ring system as shown in Fig. 7 (II). Alternatively, if this type of complex is formed, it is not sufficiently stable to be detected by shift of half-wave potential. It is more probable that, during the heating procedure, a fused ring system is formed (Fig. 7 (III)), in which the *ortho*-hydroxy group positions on the *trans* dye molecule are as nearly *cis* and coplanar as is permitted by the spatial arrangement of the aluminium bonds.

In the case of Solochrome Violet R.S. at pH 4.6 the dye: aluminium ratio has been shown[2] to be 2:1. It is therefore probable that 2 fused rings are formed, satisfying the full aluminium co-ordination number of 6 and having a three-dimensional arrangement in accord with the Werner configuration for a 6-covalent atom. The suggested arrangement is shown in Fig. 7 (IV) in which, however, three-dimensional reproduction has not been attempred.

The aluminium-Solochrome Violet complex having a dye : aluminium ratio of 3:1, shown[2] to exist at pH 6.5, cannot have this structure since it would require an impossible aluminium co-ordination number of 9. It is possible that at this pH the aluminium enters into three simple chelate rings with the azo group and one hydroxy group of each of the three dye molecules. This simple explanation is rendered doubtful, however, by our failure to prepare an analagous compound with Orange II under similar conditions, indicating that the second *ortho*-hydroxy group is still involved. Further study will be necessary before a satisfactory structure for this complex can be proposed.

The limitation of complex formation to those azo dyes which have one or two *ortho*-substituted groups has been stressed by other workers[17]. Support is lent by our failure to obtain a stable complex with benzeneazoresorcinol, in which the groups are *meta* to each other on the same ring. Further study with compounds having hydroxy groups at a variety of points is, however, necessary before conclusions can be drawn, especially in view of the structure assigned by MACNULTY AND HUNTER[20] to the aluminium-haemotoxylin lakes.

The experiments with Acid Alizarin Black SN show that the two azo groups present in the molecule reduce at slightly different potentials and that aluminium complexes with each group independently of the other. A study of the graphs in Fig. 4 shows that the rate of increase of step height with aluminium concentration is different for the two steps of half-wave potential —0.7 and —0.9 V. Much further study must, however, be done before it is possible to suggest whether this is due to different numbers of electrons transferred, or to the interference of the increasing aluminium-dye step at —0.7 V with the decreasing due step. The polarograms shown in Fig. 5 indicate that the latter explanation is the more likely and that the optimum pH for this dye reaction is in the region of 6.7. Further studies will, however, be reported later.

AUTHOR'S NOTE

Since the preparation of this series of papers for publication, two papers by DEAN AND BRYAN[21] have come to hand. These discuss some of the problems dealt with by us although with a somewhat different approach. We are evidently in broad agreement on a number of points, including some of the impossible mechanisms, but it is noted that these authors suggest a sharp increase in diffusion coefficient for the complex at pH values above 5.0, in contrast with our suggestion that a new complex species is formed. We find this difficult to reconcile with our experimental evidence for a 3:1 dye-aluminium ratio, in spite of our inability to suggest the precise structure of this molecule.

We have done little work on complexes with metals other than aluminium and we can therefore present no experimental evidence in respect of these complexes. However, the suggestion that co-ordination is always bidentate and that the azo group is not involved does not conform with the evidence of several authors who have studied the mono- and di*ortho*-substituted azo dye complexes of a number of 4 and 6 covalent metals. These authors tend to confirm that the azo group is always involved, although we are in agreement with DEAN AND BRYAN that this does not cause a visible shift in half-wave potential. This may be because, as suggested in our paper, a fused ring structure is necessary to give sufficient stability to cause a shift of half-wave potential in acid solutions. In alkaline solution the 4-co-ordinate metals may be forming complexes with the (at present unspecified) type of linkage present in our 3:1 dye-aluminium complex.

It is evident from a comparative study of these two series of papers that much further work is needed to reconcile the points of difference and lead to a complete elucidation of the mechanism of these reactions.

SUMMARY

A study of the polarographic behaviour of a number of hydroxyazo dyes in the presence and absence of aluminium is reported. This study was made in order to obtain further information regarding the structure of the complexes formed between Solochrome Violet R.S. and aluminium. The results, together with those already reported in previous papers, are discussed in relation to the reported structure of the azo dye complexes of other metals.

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Received November 5th, 1957

Short Communication

Assay of tributyl phosphate in organic solvents

The extensive use of tributyl phosphate (T.B.P.) as a solvent for uranium extractions makes it necessary to have a simple and accurate method for its assay in the presence of other organic diluents such as kerosene. Well-known methods of conversion of organic phosphorus into inorganic phosphates, either by acid digestion or by alkali nitrate fusion, followed by gravimetric or colorimetric estimation of the phosphate, have been adapted for the estimation of tributyl phosphate by DAVIES AND DAVIES[1], and of other phosphoric esters by JACOBSON AND HALL[2]. T.B.P. in kerosene has also been estimated flame-photometrically by BRITE[3].

In the following method T.B.P. is converted into inorganic ortho-phosphate by low-temperature alkali fusion, and the latter is determined titrimetrically with standard bismuthyl perchlorate. The method was standardised using synthetic solutions of dry T.B.P. in kerosene.

Dry T.B.P.: Eastman Kodak reagent grade T.B.P. was purified and dried by the method recommended by ALCOCK *et al.*[4]. Aliquots of this dry T.B.P. were suitably diluted with kerosene to give a series of standard solutions.

The preparation of the other reagents used has been given elsewhere[5].

Method

Place 2 ml of the standard solution in a 30-ml nickel crucible. Add powdered sodium hydroxide to soak and absorb the liquid completely. Finally cover the mass with a thick layer of powdered sodium hydroxide. Cover the crucible and heat slowly on a wire gauze. Increase the flame slowly in the course of the next hour so that the sodium hydroxide melts and complete the reaction by heating the crucible directly till the mass becomes homogeneous.

Dissolve the cooled mass in the minimum amount of dilute perchloric acid and make up the solution in a 250-ml volumetric flask. Pipette 100 ml of the solution into a 500-ml conical flask, neutralise the solution to litmus, add 3.5-4.0 ml 6% v/v perchloric acid and titrate against standard bismuthyl perchlorate using 5 ml of a saturated solution of diallyl dithiocarbamido hydrazine in chloroform as extraction indicator[5].

The presence of large concentrations of sodium perchlorate in the solution causes a negative titration error, which is determined by titrating a standard phosphate solution in the presence of the same amount of sodium perchlorate. This negative error is due to the high ionic strength of the solution which decreases the activity coefficient of the bismuth and phosphate ions in solution, and consequently raises the solubility of the bismuth phosphate precipitate so that a premature end point is obtained[6].

From the titre readings, calculate the T.B.P. content of the solution from the relation

$$1 \text{ mole T.B.P.} \equiv 266.6 \text{ g} \equiv PO_4^{-3} \equiv BiPO_4 \equiv 1000 \text{ ml } 1M\ Bi^{+3}.$$

As T.B.P. samples are likely to contain small amounts of uranium and nitric acid, these were added to a standard solution and the recovery of phosphate tested as given above. In the presence of such cations, the acidity of the solution was adjusted as given in a previous communication[5].

Results obtained for a number of synthetic solutions in the presence and absence of uranium are given in Table I.

TABLE I

RECOVERY OF TRIBUTYL PHOSPHATE IN THE ABSENCE AND PRESENCE OF URANIUM

Concn. of the T.B.P. taken		*Diluent — kerosene*
in % v/v	*in % w/v*[a]	*Concn. of T.B.P. recovered in % w/v*
30.00	29.07	29.52
35.00	33.84	33.94
37.50	36.41	36.32
40.00	38.61	38.45
50.00	48.29	48.16
35.00 } in presence of uranium	33.84	33.79
40.00 } and nitric acid	38.61	38.60

[a] These values were calculated from the weights of the corresponding aliquots of T.B.P. taken for dilution.

The method gives directly the concn. of T.B.P. in percentage weight/volume of the solution analysed. From the data in the 1st two columns of the Table, an average value of 0.968 is obtained for the density of pure T.B.P. at 32°, which may be used to compute the concentration of T.B.P. in percentage v/v.

It may also be noted that the analysis is based on the assay of phosphate in solution and does not take into account the presence of any acid phosphates which might be present in samples. When the presence of such products is suspected, a preliminary alkaline wash of the solution should precede the phosphate determination.

The authors wish to thank Dr. V. T. ATHAVALE for his help and guidance in the course of the work.

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Received December 9th, 1957

REVUE DE LIVRE

Das Dithizon und seine Anwendung in der Mikro- und Spurenanalyse von G. **Iwantscheff**. Verlag Chemie, G.m.b.H. Weinheim/Bergstr., 1958, Introduction du Prof. Dr. H. Fischer, 272 pp., 41 figs., 24 tables. Prix: relié pleine toile DM 29.80.

Cet ouvrage apporte aussi bien à l'analyste débutant qu'à l'analyste expérimenté un aperçu complet sur les propriétés et l'utilisation de la dithizone en chimie analytique, notamment dans les domaines de la séparation et le dosage de traces.

Son contenu, très bien présenté, débute par un compte rendu des propriétés physiques et chimiques du réactif et de ses complexes métalliques. Chapitre important lorsqu'on veut retirer le maximum de ce qu'un réactif est capable de nous offrir dans le domaine de l'analyse.

La seconde partie est consacré à la description générale des techniques de laboratoire qu'entraîne l'utilisation de la dithizone. L'auteur fait une description du matériel et des réactifs nécessaires, et insiste sur la pureté et la méthode de leur purification. Après avoir passé en revue les bases théoriques du dosage volumétrique et colorimétrique ainsi que la théorie de l'extraction, nous arrivons à la troisième partie, traitant les applications de la dithizone en chimie analytique quantitative.

La séparation et le dosage des 18 éléments suivants sont décrits: Ag, Hg, Pd, Au, Po, Cu, Bi, In, Sn, Zn, Cd, Co, Ni, Pb, Fe, Mn, Pt, Tl. Un exemple pratique d'analyse de trace, appliqué en métallurgie, est donné pour chaque élément. Ce chapitre a d'autant plus de valeur que l'auteur ne se contente pas de reproduire un mode opératoire décrit dans la littérature, mais qu'il a choisi des méthodes mises au point et éprouvées par lui-même.

Dans une quatrième partie, l'auteur commente l'utilisation du réactif en chimie analytique qualitative.

La cinquième et dernière partie est consacré aux utilisations particulières de la dithizone: indicateur pour l'analyse volumétrique par précipitation, utilisation pour la séparation et l'enrichissement de traces d'éléments en vue d'un dosage spectrographique ou polarographique, séparation chromatographique des dithizonates.

En annexe, l'auteur donne les méthodes de préparations du réactif et de ses dérivés.

En conclusion, nous pouvons ajouter que les nombreux tableaux, joints à un texte plein de clarté, viennent augmenter l'intérêt de cet ouvrage qui peut être recommandé à tout chimiste s'intéressant aux méthodes de dosages de traces. 523 références.

W. **Haerdi** (Genève)

BOOK REVIEW

Flame Photometry, by F. **Burriel-Martí and** J. **Ramírez-Muñoz**, Elsevier Publishing Company, Amsterdam, London, New York, Princeton, 1957, 531 pp., 99 figs., 30 tables, £ 3.5.–.

After a brief review of the principles and possibilities of flame photometry, the authors describe in detail the different parts of the flame photometer and the various types of instruments, thus giving the reader an opportunity of comparing them critically.

They go on to discuss the sensitivity of the determinations and the limitations of flame photometry, depending either on the instrumental system, the working conditions or the sample.

The part devoted to the experimental method explains all the necessary operations for the calibration of a flame photometer and for carrying out the experimental measurements on the samples under analysis, special attention being given to remedies for instrumental and storage troubles.

A survey of the analytical applications provides evidence for the usefulness of flame photometry for the analysis of water, agricultural and biological materials, mineral and manufactured products etc. Every analytical procedure is described, as well as the possible interferences and the preparation of samples and standards.

Although data from 578 literature references have been dealt with, this typographically well-presented book remains easy to read, thanks to the clear classification of the contents and a comprehensive subject index. It is an indispensable introduction for anyone who is planning to set up a flame photometry laboratory. It will also provide much information for the research-worker who is already familiar with the method although flame emission is only treated qualitatively.

The bibliography includes 909 references.

N. **Kemp** (Ghent)

DIRECT TITRATION OF POTASSIUM FERRICYANIDE WITH HYDRAZINE SULPHATE IN PRESENCE OF ZINC SULPHATE DETERMINATION OF HYDRAZINE

by

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While the oxidizing capacity of potassium ferricyanide especially in alkaline medium is known[1-7], its use in direct titrations has been restricted because of (1) the generally slow and incomplete reactions, (2) the low oxidation potential of the ferri-ferrocyanide system[8], $[\mathrm{Fe(CN)_6}]^{-4} \rightleftarrows [\mathrm{Fe(CN)_6}]^{-3} + e$ ($E_0 = -0.36$ V), and (3) the lack of suitable indicators for end point detection. However, if the ferrocyanide is precipitated as sparingly soluble white zinc potassium ferrocyanide, the oxidation proceeds rapidly as a result of the rise in oxidation potential of ferricyanide ion through the removal of ferrocyanide ion[7]. Thus the ferricyanide–iodide reaction which is otherwise slow and reversible takes place almost instantaneously in slightly acidic medium in the presence of a zinc salt[9]. Depending upon this principle, BHUKAROV AND PODLUBNYA[10] outlined a method for estimating glucose by titrating a hot alkaline solution of potassium ferricyanide with the reducing sugar solution containing an appropriate quantity of zinc sulphate. The end-point is indicated by complete decolorization of the solution.

The reaction between alkaline ferricyanide and hydrazine sulphate has been a subject of several investigations[3,4,11-13]. It was first employed by SUSEELA[14] for a direct titration using potentiometric end points. The purpose of the present work was to investigate the possibility of titrating potassium ferricyanide solution against hydrazine sulphate in presence of zinc sulphate.

EXPERIMENTAL

Hydrazine sulphate

An accurately weighed quantity of dry, A.R. $\mathrm{N_2H_4.H_2SO_4}$ was dissolved in water, about 4 g of pure crystals of zinc sulphate were added per 0.13 g of hydrazine sulphate and the solution diluted as desired. The strength of the hydrazine solution was checked by titration with standard $\mathrm{KIO_3}$ using chloroform as indicator[15].

$$\mathrm{N_2H_4 + KIO_3 + 2HCl \rightarrow N_2 + KCl + ICl + H_2O} \quad \ldots\ldots \quad (1)$$

Potassium ferricyanide

An aqueous solution, prepared by dissolving A.R. $\mathrm{K_3[Fe(CN)_6]}$ in water, was standardised iodometrically against sodium thiosulphate[16].

A measured portion of potassium ferricyanide solution was placed in an Erlenmeyer flask, diluted to about 50 ml and heated to boiling. Hydrazine sulphate solution containing zinc sulphate was added from the burette until complete decolorization of the solution marked the end-point.

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$$4[\mathrm{Fe(CN)_6}]^{-3} + \mathrm{N_2H_4} \rightarrow 4[\mathrm{Fe(CN)_6}]^{-4} + \mathrm{N_2} + 4\mathrm{H^+} \quad (2)$$

$$2\mathrm{K_4[Fe(CN)_6]} + 3\mathrm{ZnSO_4} \rightarrow \mathrm{Zn_3K_2[Fe(CN)_6]_2} + 3\mathrm{K_2SO_4} \quad (3)$$

Thus 1 ml 1*M*-$K_3[Fe(CN)_6]$ corresponds to 0.008013 g N_2H_4 or 0.03253 g $N_2H_4 \cdot H_2SO_4$ and 1 ml 1*M*-$N_2H_4 \cdot H_2SO_4$ is equal to 1.3170 g $K_3[Fe(CN)_6]$. Representative data for hydrazine estimation are entered in Table I.

TABLE I

DETERMINATION OF HYDRAZINE

$K_3[Fe(CN)_6]$		$N_2H_4 \cdot H_2SO_4$		$N_2H_4 \cdot H_2SO_4$ (g)		
Molarity (M)	*Volume (ml)*	*Molarity (M)*	*Volume (ml)*	*Calculated*	*Found*	*Difference*
0.007194	10	0.001332	13.50	0.002338	0.002341	0.000003
0.02650	10	0.008055	8.25	0.008645	0.008620	0.000025
0.07056	4	0.01128	6.25	0.009164	0.009185	0.000021
0.1059	5	0.01332	9.90	0.01716	0.01723	0.00007
0.02650	20	0.008055	16.50	0.01729	0.01724	0.00005
0.1059	10	0.01610	16.45	0.03445	0.03446	0.00001

TABLE II

EFFECT OF ZINC SULPHATE

4 ml 0.07056*M*-$K_3[Fe(CN)_6]$ diluted to 50 ml with water;
pH at the beginning = 6 and at the end = 2.

$ZnSO_4 \cdot 7H_2O$ added per 100 ml of hydrazine sulphate soln. (g)	*$N_2H_4 \cdot H_2SO_4$ required (ml)*	*Molarity of $N_2H_4 \cdot H_2SO_4$ (M)*	
		Calculated	*Found*
2	6.20	0.01128	0.01139
4	6.25	0.01128	0.01130
6	6.25	0.01128	0.01130
8	6.25	0.01128	0.01130
10	6.25	0.01128	0.01130

TABLE III

EFFECT OF ALKALI CONCENTRATION

4 ml 0.07056*M*-$K_3[Fe(CN)_6]$ diluted to 50 ml with water;
zinc sulphate present in the hydrazine sulphate solution = 4 g.

Overall normality of NaOH (N)	*$N_2H_4 \cdot H_2SO_4$ required (ml)*	*Molarity of $N_2H_4 \cdot H_2SO_4$ (M)*	
		Calculated	*Found*
0.0	6.25	0.01128	0.01130
0.1	6.25	0.01128	0.01130
0.4	6.25	0.01128	0.01130
0.7	6.25	0.01128	0.01130
0.8	6.25	0.01128	0.01130
0.9	6.30	0.01128	0.01121
1.2	6.33	0.01128	0.01116
1.5	a		

a End-point difficult to perceive.

DISCUSSION

The overall reaction between hydrazine and potassium ferricyanide in presence of zinc sulphate may be written as:

$$4K_3[Fe(CN)_6] + N_2H_4 + 6ZnSO_4 \rightarrow N_2 + 2Zn_3K_2[Fe(CN)_6]_2 + 2H_2SO_4 + 4K_2SO_4 \quad . \; . \; (4)$$

From this stoichiometry it follows that 100 ml of 0.01*M*-$N_2H_4 \cdot H_2SO_4$ solution (or 0.13 g hydrazine sulphate) should contain 1.722 g zinc sulphate. It was observed that while even a large excess of zinc sulphate is without any adverse effect, at least 3.544 g (*i.e.*, twice the theoretical) should be present per 100 ml of 0.01*M* hydrazine solution. (*cf.* Table II). A series of experiments revealed that before titration the ferricyanide solution may be almost neutral or up to 0.8*N* with respect to sodium or potassium hydroxide (*cf.* Table III). Hot solutions of ferricyanide in presence of mineral acids are susceptible to decomposition and should therefore be avoided. However, the acidity of aqueous hydrazine sulphate solution (pH = 2) does not affect the precise end point. In fact, successful titrations of aqueous ferricyanide solution (pH = 6) were carried out with hydrazine sulphate solution containing zinc sulphate (pH at the end point about 2). At alkali concentrations beyond 0.8*N* the results were usually faulty and the end points difficult to discern due presumably to the tendency of zinc ions to form zinc hydroxide rather than the zinc potassium ferrocyanide.

In their excellent review of methods of estimating hydrazine, PENNEMAN AND AUDRIETH[15] considered direct titrations with iodate or iodine as the best methods. They further cautioned against analyses carried out in alkaline medium in view of the atmospheric oxidation of free hydrazine. The present method is free from this error, is rapid and accurate within experimental deviation and possesses an additional advantage of not requiring an indicator. The cost involved in using ferricyanide and zinc sulphate is much less than that involved in either the iodate or the iodine method. Besides, potassium ferricyanide can serve as a standard substance and its large equivalent weight (almost 6 times that of KIO_3, *cf.* (1) and (4)) is of practical significance[17]. Since hydrazine sulphate is recommended as a standard in iodometry and acidimetry[16], its utility for the determination of ferricyanide follows.

Further work on the titrimetric estimation of substituted hydrazines, hydroxylamine and other substances oxidizable by ferricyanide is now in progress.

ACKNOWLEDGEMENT

Grateful thanks of the author are due to Professor PHILIP W. WEST for research facilities and interest in the work.

SUMMARY

Operative conditions for direct titration of potassium ferricyanide solution with a solution of hydrazine sulphate which contains zinc sulphate are described. The results are comparable with those obtained by the standard iodate procedure. The chief advantages of the present method of estimating hydrazine are (1) titration in slightly acidic medium and (2) no indicator is required. Determination of substituted hydrazines, hydroxylamine and other reducing substances on similar lines is suggested.

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Received January 14th, 1958

THE AUTOMATIC TITRATION OF PRIMARY AROMATIC AMINES WITH NITROUS ACID

by

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The diazotisation reaction $R.NH_2.HCl + HNO_2 \rightleftharpoons R.N_2Cl + 2\,H_2O$ is a well-known and widely used method of determining the primary amine group in aromatic substances: the amine is usually dissolved in dilute hydrochloric acid and standard sodium nitrite solution is added from a burette.

The end-point is taken to be when free nitrous acid persists in the titrated solution for a definite time (*e.g.* 5 min) after the last addition of titrant added in specified increments (*e.g.* 0.1 ml) towards the end of the titration, and the excess nitrous acid is usually detected by spotting on starch–iodide paper. The timed end-point is necessary because diazotisation is not instantaneous: amines diazotise at various rates and sodium or potassium bromide is frequently added to increase the rate of reaction of amines which diazotise slowly[1,2].

The appearance of free nitrous acid can also be detected potentiometrically with a platinum indicator electrode[3] or by the "dead-stop" method[4]. The electrometric methods have not been as widely used as the starch–iodide indicator, but the introduction of commercial automatic titrators based upon potentiometric and "dead-stop" end-point indication could result in a considerable reduction in the time spent on nitrite titrations in laboratories where large number are performed daily, and it was with this object in mind that the following investigation was carried out.

EXPERIMENTAL

1. *"Dead-stop" method*

The "dead-stop" end-point, so called by FOULK AND BAWDEN[5] depends on a change in the polarisation of a pair of electrodes at the equivalence point. In the original method[5] a small E.M.F. is applied to a pair of platinum electrodes immersed in the solution to be titrated; the E.M.F. is sufficient to polarise the electrodes but is not great enough to cause an appreciable current to flow between them until the polarisation of both anode and cathode have been destroyed chemically. A prerequisite of "dead-stop" titrations is, therefore, that at least one of the electrodes is polarised on one side of the equivalence point while both electrodes must be chemically depolarised on the other side, and when these conditions are satisfied the equivalence point is signalled by an abrupt change in the current flowing between the electrodes.

A variation of this method has been described by SULLY[6] in which the electrodes are placed in series with a very high resistance (3.3 megohm) and a comparatively high E.M.F. (say 1.5 V) is applied: this causes a small but virtually constant current ($< 1\ \mu$A) to flow between the electrodes throughout the titration, and the change in polarisation at the end-point is signalled by an abrupt change in the potential difference between them.

In the titration of a primary aromatic amine with nitrous acid, the cathode remains polarised until free nitrous acid is present and the anode (at least in the presence of bromide) remains depolarised throughout: the necessary conditions for a "dead-stop" titration are, therefore, satisfied.

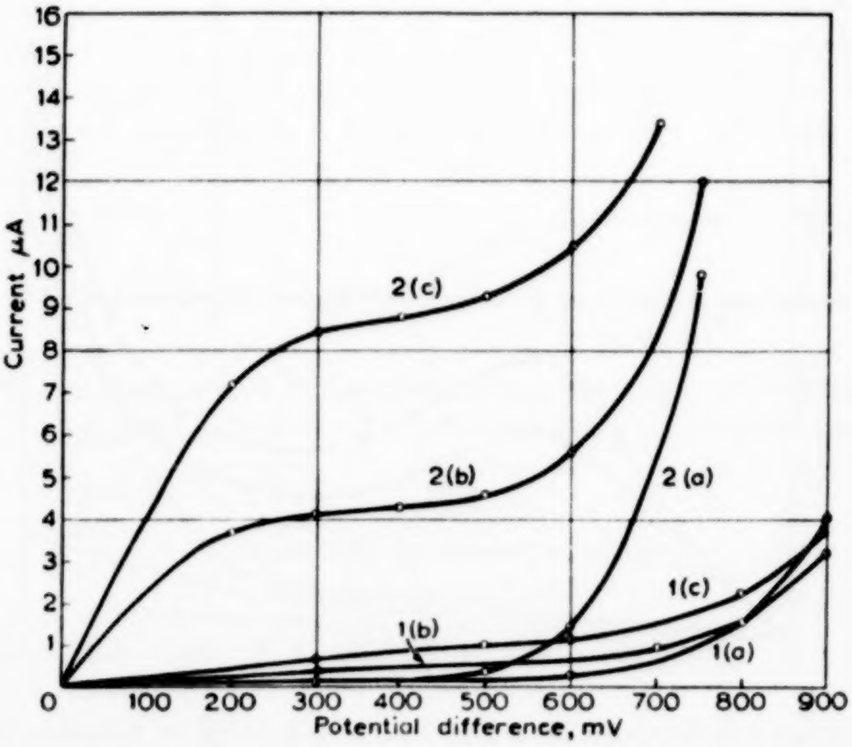

Fig. 1. Current–voltage relationships.

1(a) No $NaNO_2$, No NaBr
1(b) 0.1 ml *N*/10 $NaNO_2$, No NaBr
1(c) 0.2 ml *N*/10 $NaNO_2$, No NaBr
2(a) No $NaNO_2$, 5 g NaBr
2(b) 0.1 ml *N*/10 $NaNO_2$, 5 g NaBr
2(c) 0.2 ml *N*/10 $NaNO_2$, 5 g NaBr

Current–voltage relationship at different stages of a nitrite titration

To find out the best conditions for "dead-stop" nitrite titrations, two platinum wire electrodes (2 cm of 24 S.W.G.) were dipped into the mechanically-stirred solution, and an E.M.F. was applied by means of a potentiometer. The current flowing was measured with a galvanometer and the potential difference between the electrodes was measured with a valve potentiometer. The measurements were made with applied potential differences between 0 and 1,000 mV with the following solutions:

(i) Blanks consisting of 100 ml water, 10 ml conc. HCl, and known amounts of $NaNO_2$.
(ii) As (i) but with 5 g NaBr added.
(iii) Solutions of sulphanilamide in 100 ml water and 10 ml conc. HCl to which had been added (a) 98% and (b) 102% of the amount of *N*/10 nitrite required for complete titration.
(iv) As (iii) but with 5 g NaBr added.

The results are shown in Figs. 1 and 2, from which the following conclusions emerge:

(1) Very little current flows if there is no free nitrous acid in the solution, either in the blank, or in the presence of diazotised amine, or in the presence of NaBr.

(2) Introduction of excess nitrous acid causes, in all cases, an increase in the current, but the increase is much greater in the presence of NaBr.

(3) The increase of current caused by a given excess of nitrous acid is much greater in the blank than in the presence of diazonium salt.

The same experiments were made with *p*-nitroaniline in place of sulphanilamide, with very similar results.

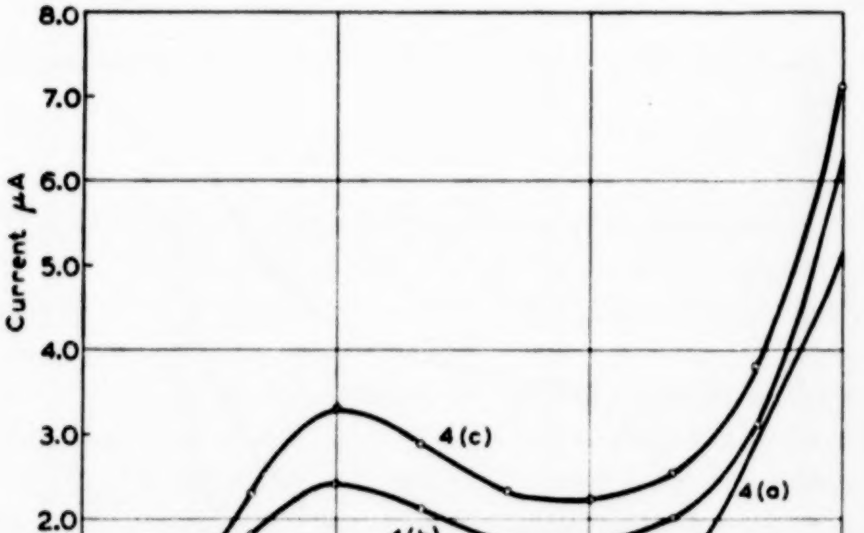

Fig. 2. Current–voltage relationships before and after end-point in titration of sulphanilamide.
3(a) Before end-point, No NaBr
3(b) Approx. 1.5 ml *N*/10 $NaNO_2$ after end-point, No NaBr
4(a) Approx. 1.0 ml *N*/10 $NaNO_2$ before end-point, 5 g NaBr
4(b) Approx. 1.0 ml *N*/10 $NaNO_2$ after end-point, 5 g NaBr
4(c) Approx. 2.0 ml *N*/10 $NaNO_2$ after end-point, 5 g NaBr

References p. 215

In order to get the best indication of the end-point (*i.e.* a large increase in current for a small excess of nitrous acid) the potential difference must be fairly large — 300 to 400 mV — and sodium bromide must be present. Alternatively, if a constant current of about 0.5 μA is used the end-point will be indicated by an abrupt fall in the potential difference between the electrodes and here again sodium bromide will greatly improve the end-point.

Titration of various primary aromatic amines

Several primary amines were titrated using a constant E.M.F. of 300 mV and amine equivalent to about 45 ml $N/10$ $NaNO_2$ dissolved in 100 ml water containing 10 ml conc. HCl and 5 g NaBr; the current was measured 1 minute after each addition of titrant, which was added 0.2 ml at a time towards the end of the titration. Good end-points, shown by a sudden increase in current, were obtained in all cases, but as will be seen from Fig. 3 (in which the current–volume graphs for sulphanilamide, *p*-nitroaniline and dianisidine are shown) the titration of dianisidine is abnormal in that a high current (1.5 μA) flows during the early part of the titration. The results are given in Table I, together with those obtained by the potentiometric and starch–iodide methods.

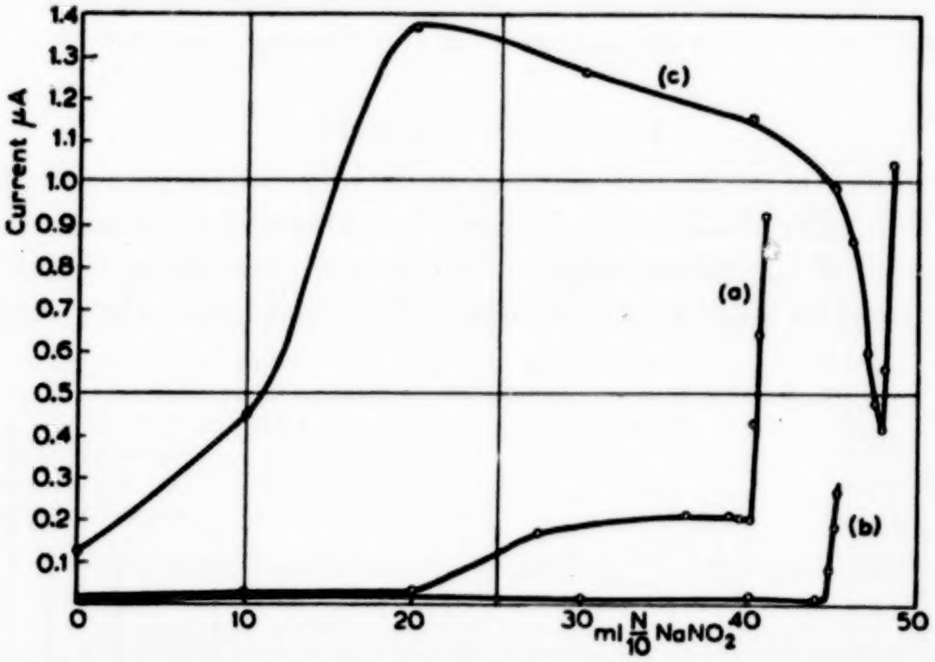

Fig. 3. Titration of primary aromatic amines, 300 mV applied.
(a) Sulphanilamide (b) *p*-Nitroaniline (c) Dianisidine

TABLE I

TITRATION OF VARIOUS AMINES

% calculated to M.W.

Amine	*M.W.*	*Starch–iodide end-point*	*"Dead-stop" end-point*	*Potentiometric end-point*
Sulphanilamide	172	99.8	99.8	99.8
p-Nitroaniline	138	99.3	99.1	99.5
Dianisidine	244	97.9	97.7	97.9
o-Anisidine	123	99.4	99.6	98.8
Mixed xylidines	121	100.0	100.0	100.1
Benzidine	184	99.4	99.6	99.8

Sulphanilamide was also titrated using a constant current of 0.8 μA; the end-point was indicated by a fall in the potential difference from 640 mV to 498 mV on the addition of 0.2 ml $N/10$ $NaNO_2$, and corresponded to a strength of 99.7% (M.W. 172).

Effect of iron and copper salts

Technical quality aromatic amines may contain metallic impurities and the effect of iron and copper salts on the titration of sulphanilamide was investigated using an applied potential of 300 mV: addition of 1 part of iron (added as ferric chloride) per 100 parts of amine increased the initial current from virtually zero to 6.6 μA; this current fell as the titration proceeded until, just before the end-point, it was 0.1 μA. The end-point was indicated, as usual, by a sudden increase in current, and the level of the results was not affected.

A similar effect was produced by addition of 1 part of copper (as copper sulphate) per 100 parts of amine.

The foregoing observations confirm that the "dead-stop" end-point can be employed as the basis for automatic titration of some primary aromatic amines with nitrous acid; for other amines (dianisidine for example) the method is not suitable because the current which passes at the beginning of the titration will shut off the titrator long before the end-point is reached. For the same reason, appreciable amounts of iron or copper salts will prevent the apparatus from functioning correctly.

2. *Potentiometric method*

Most potentiometric titrimeters add titrant rapidly until a preselected potential is reached, and then more slowly until the predetermined end-point potential is reached. The first criterion of the practicability of automatic titration is, therefore, that the end-point potential for a given substance shall be reproducible: also, in order that the

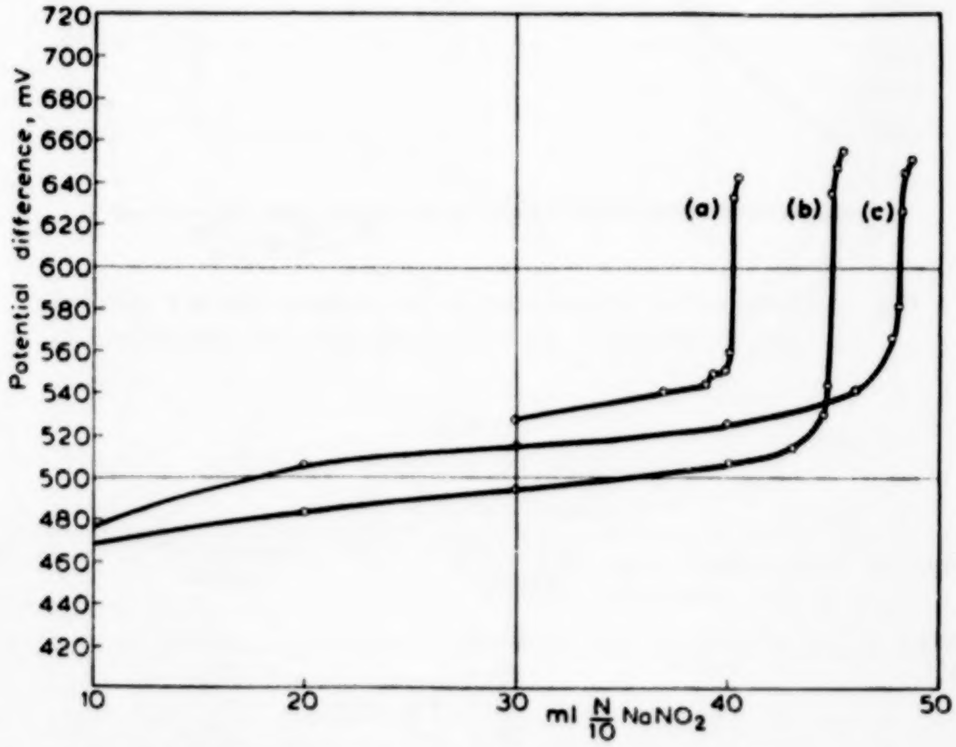

Fig. 4. Potentiometric titrations of primary aromatic amines.
(a) Sulphanilamide (b) *p*-Nitroaniline (c) Dianisidine

titration shall proceed rapidly, it is necessary that the titrant shall be absorbed quickly in the early stages.

To investigate these points, selected amines were titrated potentiometrically in hydrochloric acid solution, using a platinum indicator electrode and a saturated calomel half-cell, as follows:

(i) Allowing the potential to become constant after each addition of nitrite.

(ii) Recording the potential exactly 1 min after each addition of nitrite.

(iii) Adding nitrite rapidly, with the burette tap full open, until the observed potential was about 40 mV less than that of the inflection point obtained in (ii). Separate drops were then added until this potential was reached: if the potential remained at or above the end-point potential for 1 min the titration was assumed to be complete, but if it fell below, more nitrite was added, dropwise, until the end-point potential was maintained for 1 min after the last addition. Sodium bromide (5 g) was added in the titrations of benzidine and *o*-anisidine because these amines do not diazotise rapidly in the absence of bromide. No bromide was added in the titrations of sulphanilamide, *p*-nitroaniline or H-acid.

The results are shown in Table II and typical titration curves are shown in Fig. 4.

TABLE II

POTENTIOMETRIC TITRATIONS AT DIFFERENT RATES

Amine	*Slow titration as in (i) above*		*1 min allowed after each addition as in (ii)*		*Rapid titration to end-point potential (2) % to M.W.*
	% to M.W.	*End-point potential (1) mV*	*% to M.W.*	*End-point potential (2) mV*	
Sulphanilamide	99.5	535	99.8	610	100.0
p-Nitroaniline	99.4	600	99.5	600	99.5
Benzidine	99.1	600	99.8	610	99.6
o-Anisidine	99.4	550	98.8	600	99.6
H-acid (1,8-aminonaphthol-3,6-disulphonic acid) sodium salt technical paste	82.2	560	81.0	560	82.0

In titrations of sulphanilamide and *o*-anisidine on successive days the end-point potential varied by less than ± 10 mV; this variation had negligible effect on the titre itself.

The end-point potential and the rate of change of potential $\left(\frac{\Delta E}{\Delta V}\right)$ at the end-point varied with the concentration of HCl employed, and in order to obtain an end-point satisfactory for use with an automatic titrimeter, a concentration of HCl not less than 1*M* is desirable.

Effect of iron and copper salts

The addition of 1% iron (added as ferric chloride) and of 1% of copper (as copper sulphate) had no effect either on the level of result or on the end-point potential in titrations of *o*-anisidine.

3. *Application of automatic titrators*

The preliminary experiments described in the foregoing sections show that either the "dead-stop" or potentiometric systems can be used to control an automatic titrator in nitrite titrations, but that the potentiometric system has advantages in that (i) it is unaffected by iron or copper salts, (ii) it appears to be applicable to a greater number of amines, and (iii) addition of sodium bromide is necessary only for titrating some amines, whereas the "dead-stop" system requires it to be added for all.

The potentiometric system was, therefore, selected for further trial, and two commercial potentiometric titrimeters* were examined in the titration of sulphanilamide (which diazotises rapidly) and *o*-anisidine (an amine which diazotises slowly). These titrimeters both employ dual-speed delivery of titrant, *i.e.* at the beginning of the titration the reagent is added rapidly until a preset E.M.F. is developed by the electrode: when this happens, the fast-rate valve is closed, and remains closed for the rest of the titration. The slow-rate valve remains open, and dropwise addition of reagent is continued until the pre-determined end-point potential is reached. At this point the slow-rate valve closes also, and remains so until the potential of the electrode falls below the end-point potential. If the potential does fall in this way, the slow valve opens and admits an increment of reagent, and this cycle is repeated until the potential of the indicator electrode remains *permanently* at or above the end-point potential. (Some automatic titrators include a device which prevents the slow valve from opening again if it remains closed for a fixed period of, say, 30 sec, but the Pye and E.I.L. titrators used in this work do not have this device.)

The results obtained with these two instruments are given in Table III.

TABLE III

TITRATIONS WITH AUTOMATIC TITRIMETERS

Instrument	*Pye*		*E.I.L.*	
Amine	%	*Time taken to complete titration min*	%	*Time taken to complete titration min*
Sulphanilamide (by manual titration with starch–iodide indicator = 99.8%)	99.8	3	100.0	5
	99.8	4	100.0	3
	99.7	3	99.8	3
	99.7	5	100.0	4
	99.6	4		
	99.7	4		
o-Anisidine (by manual titration with starch–iodide indicator = 99.5%)	99.6	5	99.7	10
	99.4	9½	99.3	9½
	99.6	6	99.5	6
	99.5	7	99.4	8½
	99.5	4		
	99.2	5½		
	99.2	8		
	99.1	8		
	99.6	11½		

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* The Pye Automatic Titrator and The Electronic Instruments Limited Automatic Titrimeter.

Discussion of results

The reproducibility of the titrations carried out by the instruments is certainly as good as would normally be obtained in manual titrations; in fact, subsequent experience suggests that in many cases the machine is appreciably more precise than a human operator. The time taken by the machine to complete a single titration depends very much upon the setting of the control which shuts off the fast delivery of titrant, and the optimum setting for a given amine on a particular instrument must, of course, be found by trial and error. The end-point potential also varies somewhat from one amine to another (Table II) and must be established by preliminary experiment: the most advantageous application of the titrimeter will, therefore, be in laboratories where repetitive analysis of a limited range of amines must be carried out.

Procedure

The following is the procedure which has been successfully used with commercial titrators.

Take an aliquot of amine solution containing amine equivalent to about 40 ml $N/10$ $NaNO_2$, dilute to 100 ml with water and add 10 ml conc. HCl. In the titration of amines which diazotise slowly add 5 g sodium bromide. Stir with an efficient mechanical stirrer and titrate at 15°–20°C with $N/10$ $NaNO_2$ using a platinum indicator electrode and a saturated calomel reference electrode (connected to the solution by means of a saturated KCl bridge) until the predetermined end-point potential is maintained for 1 min after the last addition of titrant. Set the instrument so that the fast addition of titrant is stopped at about 20–30 mV before the end-point potential is reached.

The potentials used for the end-point setting and for the fast/slow change may vary to some extent with the platinum electrode and instrument used: they must also be established independently for each amine titrated. Therefore, for any given titration it is necessary to establish the correct end-point by means of a preliminary titration using starch–iodide papers (or a manually operated potentiometer) to detect the equivalence point.

SUMMARY

The "dead-stop" and potentiometric systems have been compared as a basis for the automatic titration of primary aromatic amines with nitrous acid; either system can be used but the potentiometric method is more widely applicable and is less subject to interference. Titrations of sulphanilamide and *o*-anisidine have been made with two commercial titrimeters and with both instruments the results obtained were at least equal in precision to those which would normally be obtained in manual titrations.

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Received November 27th, 1957

DETERMINATION OF DIETHYL AND DIBUTYL PHTHALATES IN PROPELLANTS

by

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INTRODUCTION

The determination of diethyl and dibutyl phthalates in propellants containing nitroaromatic compounds, nitroesters, and stabilizers is a difficult matter. The usual saponification methods[1] or gravimetric methods whereby insoluble dipotassium phthalate alcoholate is precipitated[2,3] are not applicable in the presence of nitro compounds. The alkali used in these methods reacts with nitroaromatic compounds to form complex substances such as azoxybenzene derivatives[4]. Alcoholic potassium hydroxide reacts with nitroglycerin to form potassium acetate, potassium formate, potassium nitrate and potassium nitrite[5]. The polarographic method for the determination of phthalates[6] cannot be used in the presence of nitro compounds, since the reduction waves of nitro compounds overlap with the reduction waves of phthalates. The ultraviolet method for the determination of phthalates[7,8] is not applicable in the presence of nitro compounds because these compounds show strong absorption at the wavelengths used for phthalates.

PREVIOUS METHODS

The following methods have been used for the determination of diethyl and dibutyl phthalates in propellants containing nitro compounds (after a preliminary extraction to separate the phthalate from nitrocellulose):

1. Reduction of the nitro compounds by shaking 15 min with ammonium sulfide solution, followed by extraction of the phthalate with petroleum ether. The petroleum ether extract is washed with sodium chloride solution and is treated with mercury to eliminate sulfur compounds. The phthalate is then determined by saponification[9].
2. Reduction of the nitro compounds by boiling with ferrous chloride in an alcoholic hydrochloric acid solution. The phthalate is then extracted with ether, the ether layer washed with sodium sulfate solution to remove iron, and the phthalate determined by saponification[10].
3. Reduction of the nitro compounds by heating with titanous chloride solution in an acetic acid medium. The phthalate is then extracted with petroleum ether and determined by saponification[11].
4. Polarographic determination after reduction of the nitro compounds by zinc in a sulfuric or acetic acid medium, or by catalytic hydrogenation in the presence of platinum oxide as a catalyst[12].
5. Reduction of the nitro compounds by zinc in an acetic acid medium followed by extraction with methylene chloride. The solvent layer is washed with potassium carbonate solution and the phthalate precipitated as dipotassium phthalate alcoholate

which is filtered. The determination is finished gravimetrically, or the precipitate is dissolved in glacial acetic acid and titrated with perchloric acid using crystal violet indicator[13]. This method gives high results when applied to propellants containing more than 5% dinitrotoluene.

6. Reduction of the nitro compounds with zinc in an acetic acid medium followed by extraction with methylene chloride. The solution is saponified, diluted, and the interfering substances extracted with isopropyl ether. The potassium phthalate in the aqueous solution is then treated with hydrochloric acid and the resultant phthalic acid determined by ultraviolet[14].

7. Chromatographic separation of the phthalate from nitro compounds followed by gravimetric, polarographic, or ultraviolet determination of the phthalate[15,16].

8. Reduction of the nitro compounds with zinc followed by oxidation of the aliphatic chain with nitric acid. Any oxalic acid formed by oxidation of the cellulose is eliminated by the addition of permanganate, and lead acetate is added to precipitate the phthalate as lead phthalate. The latter substance is dissolved in nitric acid and the lead determined as lead sulfate[17].

9. Dissolution of the entire sample by heating with potassium hydroxide solution and hydrogen peroxide. This decomposes the nitrocellulose and nitroglycerin and breaks down the phthalate into potassium phthalate and the corresponding alcohol (ethyl), which is then distilled as a low boiling azeotrope of benzene, alcohol and water. The alcohol in the distillate is titrated with dichromate[15,18].

10. Infra red methods[19].

11. By difference[15]. Although subject to obvious errors, this method of determining phthalates is widely used. SANDHOFF AND KIGHT[20] state, "In a number of instances it is quite possible that this method will be more accurate than most of those proposed."

A Phthalate Committee under the auspices of the Joint Army, Navy and Air Force Panel on the Analytical Chemistry of Solid Propellants made a study of the above methods and found that they left much to be desired[20]. The Committee recommended that an improved method be developed[20]. This laboratory undertook to develop such a method.

DEVELOPMENT OF IMPROVED METHOD

As a first step in the development of an improved method the effect of various reducing agents on the types and amounts of nitro compounds found in propellants was investigated. Ammonium sulfide was found to be effective as a reducing agent but it was very obnoxious to handle. Also, it produced with some propellant compositions interfering mercaptan type compounds which could not be eliminated by treatment with mercury, and which interfered with the saponification. Titanous chloride was found to produce erratic results for diethyl and dibutyl phthalates when more than small amounts of dinitrotoluene were present. This same conclusion was arrived at independently by work at Picatinny Arsenal. The source of the difficulties with the titanous chloride was the hydrolysis of the titanium and the partial destruction of the phthalate during the heating that was necessary to reduce the dinitrotoluene completely. It was found that ferrous chloride, either in an alcoholic, alcoholic hydrochloric acid, or an acetic acid medium could only reduce very small amounts of dinitrotoluene. The same was true of vanadous solution[21], chromous solution[4], molybdic solution[22], and stannous chloride solution[23]. No experiments were conducted with electrolytic reduction[4]. However, from observations of DEGERING[4] electrolytic reduction of nitro compounds would not be expected to be quantitative. Catalytic hydrogenation[4,12] was not considered, since this reduction process was time-consuming and required special equipment. The reagent that seemed to offer the most promise for reducing nitro compounds was zinc. Therefore, efforts were directed towards perfecting that means of reduction.

Previous investigators have used zinc in an acetic acid medium or a sulfuric acid medium. The use of a sulfuric acid medium seemed to cause hydrolysis of the phthalate so an acetic acid medium seemed preferable. Previous investigators used moderate temperatures and rather concentrated acetic acid solutions. The time required for the reduction was 15 min to 2 h. It was found in this laboratory that if the zinc was added to a 60% acetic acid solution at about 95°C, and the solution boiled gently, complete reduction of nitro compounds took place in 5 min. The effect of temperature is readily illustrated by experiments with dinitrotoluene. When the acetic acid solution of that compound was heated with zinc at about 90°C on the steam bath the solution changed immediately from colorless to blue. In about an hour it started to change to brown, the final color obtained. When the acetic acid solution of the dinitrotoluene was boiled gently with the zinc, the solution changed from blue to brown in 3 min and to a bright yellow in 5 min. The blue color and possibly the brown colors represent intermediate reduction steps, possibly nitrosobenzene and phenylhydroxylamine derivatives[24]. They could also represent reduction of one nitro group at a time. The final reduction product is the diamino compound. Nitroglycerine would be expected to be reduced only to glycerine by zinc and acetic acid[5].

The acidity of the acetic acid used in the reduction of the nitro compounds was important. A 60% concentration was found to be best. Too concentrated solutions caused slow and incomplete reduction. Too dilute solutions would not dissolve the nitro compounds completely. The amount of acetic acid recommended, 35 ml, was also important. If too much were used, a significant amount of acetic acid was subsequently extracted, necessitating neutralization of the acetic acid in the petroleum ether. This neutralization has been accomplished by the addition of up to several ml of alcoholic potassium hydroxide solution[11] or by shaking with potassium carbonate solution[13]. In the proposed method 1 to 3 drops of alcoholic potassium hydroxide was found to be sufficient to neutralize the acetic acid prior to the saponification.

Carefull

After the reduction, the solution was diluted and extracted three times with petroleum ether. The petroleum ether was evaporated off and the phthalate determined by saponification. Petroleum ether was preferable to other solvents for the extraction. Ethyl ether was not entirely satisfactory because much of it dissolved in the dilute acetic acid, as indicated by the decrease in volume of the ethyl ether after the extraction. Also, the ethyl ether seemed to extract some unknown substance that caused difficulties with saponification. Carbon tetrachloride and methylene chloride have been suggested as extraction agents for phthalates because they have the advantage of being heavier than water in contrast to petroleum ether and ethyl ether. However, these solvents are not to be recommended when the phthalate is to be determined volumetrically, since both of these substances react with alcoholic potassium hydroxide solution. It should never be assumed that all of the solvent can be driven off by heating on the steam bath. When 2 ml of carbon tetrachloride was treated with 10 ml of ethyl alcohol and saponified as in the method, a result equivalent to 0.1590 g ethyl phthalate was obtained. When 2 ml of methylene chloride was saponified a result equivalent to 0.0542 g ethyl phthalate was obtained. Two ml of petroleum ether or 2 ml of ethyl ether were found not to react with the alkali at all.

An alcoholic potassium hydroxide solution containing 10% water was used for the saponification as suggested by Lamond[9]. This prevented the formation of caked potassium diphthalate alcoholate around the sides of the flask during the refluxing. It was thought that this caked salt could occlude some unreacted phthalate. It has been stated that a little water increases the speed of saponification[25]. All determinations were made using pyrex flasks. The attack of the pyrex was slight and superficial, since the normality of the alcoholic potassium hydroxide solution during the saponification was about 0.22*N*. Alkali resistant flasks (Corning Glass Works) could have been used.

The final problem to be considered was the solvent to be used for the extraction of the phthalate from the propellant. Four solvents have been recommended for this purpose: acetic acid (84%)[11,26], ethyl ether[9,10], methylene chloride[15], and carbon tetrachloride[15]. The acetic acid extraction was troublesome because some nitrocellulose dissolved[26]. Also, the concentration and amount of acetic acid needed was unsatisfactory for reduction with zinc. It was found that methylene chloride and carbon tetrachloride were undesirable, because the solvent that remained after the evaporation was extracted by the petroleum ether, and caused high results for the saponification. It would be expected that carbon tetrachloride would be reduced to methylene chloride and chloroform by the zinc and acetic acid[27]. Methylene chloride would be largely unaffected by the zinc and acetic acid although a small amount of methane might be produced[27]. The logical solvent for the extraction of phthalate from the propellant seemed to be ethyl ether. Excellent results were obtained using ethyl ether and a 5-g sample. Anhydrous ethyl ether is recommended because regular ether frequently contains aldehydes and other impurities that can cause high results for the saponification.

The proposed method is more rapid and trouble-free than any procedure yet proposed for the determination of ethyl and dibutyl phthalates. For reasons not clear it did not give entirely satisfactory results for dimethyl, dioctyl and diphenyl phthalates. However, this is not a serious drawback since diethyl and dibutyl phthalates are by far the most common phthalates present in propellants. Phthalates differ markedly in many of their properties such as ease of hydrolysis and solubility, and it is believed that a universal method applicable to all phthalates may not be feasible.

REAGENTS

Acetic acid, 60%. Mix 600 ml glacial acetic acid and 400 ml water.

Alcoholic potassium hydroxide solution (approximately 0.45*N*). Add 25 g of cp potassium hydroxide pellets to a mixture of 600 ml of 95% ethyl alcohol and 50 ml of water contained in a liter pyrex bottle. Swirl occasionally until dissolved. Filter through a No. 41 Whatman filter paper into a 1-liter pyrex bottle. Dilute to about 1 liter with 95% ethyl alcohol and cover with a tight fitting rubber stopper.

0.1 N hydrochloric acid. Prepare by diluting 1 *N* or 0.5 *N* hydrochloric acid that has been accurately standardized.

Phenolphthalein indicator. Dissolve 1 g of phenolphthalein in a mixture of 125 ml of 95% ethyl alcohol and 125 ml of water.

Petroleum ether, boiling point 30 to 60°C, ACS purity[28].

Ethyl ether, anhydrous, analytical reagent.

Zinc dust, Fisher Scientific Co.

PROCEDURE

Place 5 g of the sample in a paper extraction thimble and extract overnight in a Soxhlet apparatus with 125 ml of anhydrous ethyl ether. Use a 250-ml Erlenmeyer flask as a receiver. Remove the receiver and evaporate off the ether by heating on the steam bath.

Weigh out 6 g of zinc dust. Add 35 ml of 60% acetic acid to the flask containing the phthalate and heat just to incipient boiling at moderate heat. Remove the flask from the hot plate, swirl and add a small portion of zinc dust. Swirl again and continue adding the zinc until the 6 g have been added. Cover with the same watch glass, return to a cooler part of the hot plate and heat for exactly 5 min so that the solution effervesces strongly. Swirl the flask frequently during this period. Be sure that the solution effervesces strongly during the 5-min period but do not heat at more than gentle heat. Remove the flask from the hot plate and cool to room temperature in a water bath. After the solution is cool, wash down the cover lid and direct a stream of water from the wash bottle so as to wash down any loose zinc. Add 200 ml of water, swirl, allow to settle for a moment and decant the solution into a 500-ml separatory funnel, leaving the zinc in the flask (a little zinc in the separatory funnel will do no harm). Add 50 ml of water to the flask, swirl, allow to settle and decant into the 500-ml separatory funnel. Repeat with another 50 ml of water. Add 60 ml of petroleum ether to the flask, swirl, allow to settle and decant. Repeat with a second portion of petroleum ether. Shake the contents of the separatory flask for a minute and allow the layers to separate. Drain off the aqueous solution into a clean 400-ml beaker, while swirling the separatory funnel occasionally. Allow about 0.5 ml of the petroleum ether to drain off with the aqueous solution. Decant the petroleum ether layer through the top of the separatory funnel into a clean dry 250-ml Erlenmeyer flask with a ground glass joint, allowing about 0.5 ml of solution to remain in the separatory funnel. Wash the contents of the 400-ml beaker back into the separatory funnel. Add 60 ml of petroleum ether to the original flask containing the zinc and decant into the separatory funnel. Extract as before and then repeat with a third 60-ml portion of petroleum ether. Evaporate the combined extracts on the steam bath to drive off the petroleum ether.

Add 10 ml of 95% ethyl alcohol around the sides of the flask, swirl, and add 3 or 4 drops of phenolphthalein indicator. Cool. Add alcoholic potassium hydroxide (approximately 0.45N) dropwise with a medicine dropper until the solution is just pink, and then add 0.1 N hydrochloric acid dropwise with a medicine dropper until the pink color just disappears. Add by a means of a delivery pipet exactly 10 ml of alcoholic potassium hydroxide solution and reflux for 40 min under a water condenser. If salts precipitate during the refluxing, add a few drops of water from a wash bottle through the top of the condenser. At the end of the refluxing period add 50 ml of water through the top of the condenser, and remove the flask. Cover with a watch glass and cool to room temperature in a water bath. Add another 3 or 4 drops of phenolphthalein indicator and titrate with 0.1 N hydrochloric acid to the disappearance of the pink color. Run a blank titration by neutralizing 10 ml of the alcohol as described above, adding 10 ml of the alcoholic potassium hydroxide solution and refluxing for 40 min.

Calculate the percent of diethyl or dibutyl phthalate as follows:

$$\%\ \text{Diethyl phthalate} = \frac{11.11\ (B-S)N}{W}$$

or

$$\%\ \text{Dibutyl phthalate} = \frac{13.92\ (B-S)N}{W}$$

where:

B = ml of hydrochloric acid for blank titration
S = ml of hydrochloric acid for titration of sample
N = normality of hydrochloric acid
W = weight of sample

Remove the zinc that adheres to the sides of the flask by rinsing with dilute hydrochloric acid (1 to 1). Occasionally add a little dilute hydrofluoric acid (1 to 3) to the flasks and allow to soak for a few minutes to remove the superficial etching produced by the alkali.

RESULTS AND INTERFERENCES

The results obtained for diethyl and dibutyl phthalates in synthetic mixtures dissolved in 35 ml of 60% acetic acid and carried through the reduction procedure are shown in Tables I and II respectively. The results obtained for dibutyl phthalate in a typical double base powder containing nitroglycerin, dinitrotoluene, ethyl centralite and diphenylamine are shown in Table III.

TABLE I

RESULTS FOR DIETHYL PHTHALATE IN SYNTHETIC MIXTURES

Diethyl phthalate present (g)	*Other compounds present (g)*	*Diehtyl phthalate found (g)*
0.2016	—	0.2020
—	0.3 dinitrotoluene	0.0000
0.1870	0.3 dinitrotoluene	0.1872
—	0.2 ethyl centralite	0.0000
0.1902	0.2 ethyl centralite	0.1910
0.2150 0.2106 0.2089	0.3 dinitrotoluene 0.2 ethyl centralite 0.2 diphenylamine	0.2156 0.2106 0.2094
0.1994	0.3 dinitrotoluene 0.2 ethyl centralite 0.2 nitrodiphenylamine	0.1995
—	0.2711 triacetin	0.0490
0.2052	0.2060 triacetin	0.2316
0.2002	0.2122 triacetin 0.3 dinitrotoluene 0.2 ethyl centralite 0.2 diphenylamine	0.2206
—	0.2000 sucrose octaacetate	0.0160
0.2085	0.2000 sucrose octaacetate 0.3 dinitrotoluene 0.2 ethyl centralite 0.2 diphenylamine	0.2193
—	0.1489 dimethyl sebacate	0.1417[a]
0.2097	0.2228 dimethyl sebacate 0.3 dinitrotoluene 0.2 ethyl centralite 0.2 diphenylamine	0.4275[b]
—	0.2362 ethylene carbonate	0.0000
0.2102	0.2565 ethylene carbonate 0.3 dinitrotoluene 0.2 ethyl centralite 0.2 diphenylamine	0.2016

[a] 0.1466 calculated as dimethyl sebacate
[b] 25 ml of alcoholic KOH used

The following very common constituents of propellants did not interfere with the method: nitrocellulose, nitroglycerin, dinitrotoluene, diphenylamine, nitrodiphenylamine, and ethyl centralite. Experiments were conducted with the latter substance to find out whether it could react with alcoholic potassium hydroxide. It was found that when 0.2 g of ethyl centralite was dissolved in 10 ml of alcohol and saponified, a titration equivalent to 0.8 ml of 0.1 N hydrochloric acid was obtained (B—S in equation). It would seem that the ethyl centralite (diphenyldiethylurea) is either hydrolyzed by the boiling or remains largely unextracted by the petroleum ether. As can be seen from Tables I and II the presence of approximately 0.2 g of triacetin produced

TABLE II

RESULTS FOR DIBUTYL PHTHALATE IN SYNTHETIC MIXTURES

Dibutyl phthalate present (g)	Other compounds present (g)	Dibutyl phthalate found (g)
0.2273	—	[illegible]
0.2088	0.3 dinitrotoluene	[illegible]
0.2403	0.2 ethyl centralite	[illegible]
0.2234	0.3 dinitrotoluene 0.2 ethyl centralite 0.2 diphenylamine	[illegible]
0.2558		[illegible]
0.2066		[illegible]
0.2110	0.3 dinitrotoluene 0.2 ethyl centralite 0.2 nitrodiphenylamine	[illegible]
0.1931		[illegible]
0.2157		[illegible]
0.1914	0.2104 triacetin 0.3 dinitrotoluene 0.2 ethyl centralite 0.2 diphenylamine	[illegible]
0.2011	0.2000 sucrose octaacetate 0.3 dinitrotoluene 0.2 ethyl centralite 0.2 diphenylamine	[illegible]

TABLE III

RESULTS FOR DIBUTYL PHTHALATE IN A TYPICAL DOUBLE BASE POWDER (NITROCELLULOSE, NITROGLYCERINE, DINITROTOLUENE, ETHYL CENTRALITE, AND DIPHENYLAMINE)[a]

5.06	5.06	5.09	5.06	5.06	5.06

[a] Result by difference = 5%

results for diethyl and dibutyl phthalates that were about [illegible] too high. The presence of approximately 0.2 g of sucrose octaacetate produced results that were about 0.5% too high. Both of these substances are saponifiable quantitatively, so they must have been partially hydrolyzed by the boiling, or incompletely extracted by the petroleum ether. Dimethyl sebacate was carried through the procedure and saponified almost quantitatively. In fact, the method might constitute a means for determining dimethyl sebacate in the presence of nitro compounds. Ethylene carbonate did not interfere with the method, probably because of hydrolysis during the boiling. Ethylene carbonate reacts with alcoholic potassium hydroxide solution. When 0.2 g of this substance was saponified, a titration equivalent to 18 ml of 0.1 N hydrochloric acid was obtained. Glycerine formed by the reduction of nitroglycerine did not interfere. This glycerine would be expected to remain largely unextracted by the petroleum ether[28], but even if a little were extracted it would not interfere since it is not saponifiable. Glycerine cannot react with acetic acid to form glycerol acetate (a saponifiable compound) except in a non-aqueous medium[29].

The above figures for interfering substances assumed complete extraction of these substances from the propellant by ethyl ether. The following would be quantitatively extracted by the ethyl ether: nitroglycerin, dinitrotoluene [illegible], diphenylamine, ethyl centralite, triacetin, dimethyl [illegible]. Sucrose octaacetate would probably be only partially [illegible]. The [illegible] effect of a continuous ether extraction on sucrose octaacetate [illegible] propellant [illegible] difficult to judge without a standard propellant [illegible]. [illegible] salts that might be present in propellants (potassium [illegible] nitrate, ammonium nitrate, calcium carbonate, [illegible]) [illegible] extracted and would not interfere. This would [illegible] constituents [illegible] use.

SUMMARY

A rapid and accurate method [illegible] the determination of [illegible] and dibutyl phthalates in propellants [illegible] compounds [illegible] stabilizers and other substances. The phthalates [illegible] ether and [illegible] are reduced by boiling gently with [illegible] and volume of the acetic acid [illegible] phthalate [illegible] the acetic acid solution with potassium [illegible] colorimetrically. [illegible] the determination of phthalates [illegible], and a detailed study has been made of interfering compounds found in [illegible].

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Received November 26th, 195[illegible]

THE SOLVENT EXTRACTION OF ZINC WITH DITHIZONE

by

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INTRODUCTION

In 1949, IRVING AND WILLIAMS[1] presented the following equation to describe solvent extraction phenomena in a two-phase system made up of an aqueous phase containing a metal ion and hydrogen ion, and a non-aqueous phase containing a chelating agent which would complex with the metal ion.

$$E = \frac{P_r{}^n \cdot K_r{}^n \cdot [\mathrm{HR}]^n}{P_c \cdot P_r{}^n \cdot K_r{}^n \cdot [\mathrm{HR}]^n + P_c \cdot K_c \cdot [\mathrm{H}]^n} \quad \text{. . . . . . . (1)}$$

In this expression, E is defined as the ratio of total metal concentration in the non-aqueous phase to that of the aqueous phase, $[\mathrm{HR}]$ represents the concentration of chelating agent in the non-aqueous phase, $[\mathrm{H}]$ represents the concentration of hydrogen ion in the aqueous phase, n represents the number of chelating agent molecules attached per metal ion in the metal chelate, P_r represents the partition constant and K_r the ionization constant of the chelating agent, P_c represents the partition constant and K_c the dissociation constant of the metal chelate. When the term P_c is quite small (as it often is), this equation simplifies as follows:

$$E = \frac{(P_r \cdot K_r)^n \cdot [\mathrm{HR}]^n}{P_c \cdot K_c \cdot [\mathrm{H}]^n} = \frac{K \cdot [\mathrm{HR}]^n}{[\mathrm{H}]^n} \quad \text{. . . . . . . (2)}$$

When the concentrations of the total metal in the two phases are equal, E has a value of 1, and the pH corresponding to such a condition is called the $\mathrm{pH}_{1/2}$. The logarithmic form of eqn. (2) indicates that a plot of log E against (log $[\mathrm{HR}]$ + pH) should yield a straight line with a slope of n and an intercept of log K. From a consideration of eqn. (2), for two systems which differ only in the non-aqueous solvent, K_r and K_c will remain unaffected, and thus E should depend on P_r and P_c. Since these partition coefficients will probably be related to the solubilities of chelating agent and metal chelate in the non-aqueous solvent, the following equation may be written

$$\frac{[\mathrm{H}]^n}{[\mathrm{H}']^n} = \frac{(S_r'/S_r)^n}{S_c'/S_c} \quad \text{. . . . . (3)}$$

where S_r and S_c represent the solubilities of chelating agent and metal chelate in one non-aqueous solvent, and S_r' and S_c' represent these values in another non-aqueous solvent, when the two values of E are the same.

THE SYSTEM

For this series of studies, zinc was chosen as the metal ion, dithizone as the chelating agent, and several non-aqueous solvents were used. Several previous investigators, KOLTHOFF AND SANDELL[2] and IRVING, BELL, AND WILLIAMS[3], used chloroform and carbon tetrachloride as the non-aqueous phase, extracting from buffered aqueous solutions. This research involved a study of the effects of aqueous-phase complexing agents and of various non-aqueous solvents on the extraction of zinc dithizonate, as well as a study of the spectrum of zinc dithizonate in various non-aqueous solvents.

RESULTS AND INTERPRETATION

The extraction curves

The results of the extraction studies are presented in Table I. In all cases the zinc concentration in the original aqueous phase was $10^{-5}M$, and the dithizone concentration in the original non-aqueous phase was $1.8 \cdot 10^{-3}M$. All curves with the exception of those run with nitrilotriacetic acid (NTA) exhibited a shape similar to that of the typical S-shaped pattern shown by systems of this type when percentage metal extracted is plotted against the pH value of the aqueous phase. The slopes ($\Delta\%$ extracted/ΔpH) of all curves, with two exceptions, as determined between 30% and 70% extraction, showed values of 100 ± 20 agreeing with the predicted slope of 115 for a 1:2 zinc-dithizone complex. The slopes of the curves for extraction from citrate solutions were 50 and 40 for citrate concentrations of $0.01M$ and $0.1M$ respectively, and the slopes for NTA extractions were 50 and 20 at NTA concentrations of $0.001M$ and $0.01M$ respectively. The curve describing the extraction from $0.001M$ NTA solution rose from 0% extraction at a pH of 6.0 to 75% extraction at a pH of 5.0, remained there to a pH of 6.0, then dropped to 30% extraction at a pH of 7.0. The curve describing the extraction from $0.01M$ NTA solution rose from 0% extraction at a pH of 2.3 to 65% extraction at a pH of 8.0.

Interpretation of extraction curves

Previous investigators[2,3] have reported values of 3–8 for K in the chloroform extraction from a solution buffered with a small amount of phthalate. One investigation[3] reports a K-value of 97 for a $0.005M$ phthalate extraction with carbon tetrachloride and a value of 66 when the ionic strength of the solution is brought up to 0.1 with an inert salt. Another report[4], which has been strongly questioned[3], shows a value of 4 for carbon tetrachloride extraction. Our results agree with the former values. BABKO AND PILIPENKO[5] report a value of about 10^{-20} for the instability constant of zinc dithizonate, and we have obtained the same result.

In the studies with aqueous complexing agents, it was found that in the chloroform system the following ions had little effect on the shape or location of the extraction curves: chloride, bromide, thiocyanate, and acetate. However, phthalate, citrate, oxalate, EDTA, and NTA ions all altered the shape and/or the location of the curves when chloroform extractions were made. The phthalate ion caused the curve to shift

TABLE I

RESULTS OF EXTRACTION STUDIES[a]

Non-aqueous phase	*Anion in the aqueous phase*[b]	*Concentration of the anion (M)*	$pH_{\frac{1}{2}}$	K
Chloroform	Perchlorate	0.10	3.5	$3 \cdot 10^{-2}$
	Iodide	0.10	–[c]	–
	Bromide	0.10	3.5	$3 \cdot 10^{-2}$
	Thiocyanate	0.10	3.5	$3 \cdot 10^{-2}$
	Acetate	0.01	3.6	$2 \cdot 10^{-2}$
		0.10	3.6	$2 \cdot 10^{-2}$
	Chloride	0.10	3.6	$2 \cdot 10^{-2}$
	Citrate	0.01	3.9	$5 \cdot 10^{-3}$
		0.10	5.9	$5 \cdot 10^{-7}$
		1.00	6.7	$1 \cdot 10^{-8}$
	Oxalate	0.01	4.3	$8 \cdot 10^{-4}$
		0.20	5.3	$8 \cdot 10^{-6}$
	NTA[d]	0.001	4.2[e]	$1 \cdot 10^{-3}$[e]
		0.01	7.0[e]	$3 \cdot 10^{-9}$[e]
	EDTA[f]	0.001	–[g]	–
		0.01	–[g]	–
	Phthalate	0.01	2.7	$1 \cdot 10^{0}$
Carbon Tetrachloride	Perchlorate	0.10	1.9	$5 \cdot 10^{1}$
	Bromide	0.10	1.9	$5 \cdot 10^{1}$
	Citrate	0.01	2.0	$3 \cdot 10^{1}$
		0.10	2.0	$3 \cdot 10^{1}$
	EDTA[f]	0.001	–[g]	–
Benzene	Perchlorate	0.10	2.3	$8 \cdot 10^{0}$
	Citrate	0.01	2.4	$5 \cdot 10^{0}$
Chlorobenzene	Perchlorate	0.10	2.1	$2 \cdot 10^{1}$
Dichloromethane	Perchlorate	0.10	2.7	$1 \cdot 10^{0}$

[a] In all cases the zinc concentration in the original aqueous phase was $10^{-5}M$, and the dithizone concentration in the original non-aqueous phase was $1.8 \cdot 10^{-3}M$.

[b] All solutions were made up to an ionic strength of 0.10 with sodium perchlorate if necessary.

[c] Reproducible results were difficult to obtain with the iodide ion.

[d] Nitrilotriacetic acid.

[e] See text for qualifications on these values.

[f] Ethylenediaminetetracetic acid.

[g] None or very little of the zinc ion could be extracted at any pH between 1.0 and 8.0.

in a direction opposite to that expected when aqueous complexing takes place. It was suspected that zinc phthalate might be extracting, but experiments in the absence of dithizone disproved this. No explanation for this anomalous behavior can be offered. Both citrate and oxalate moved the extraction curve to higher pH values than that for the perchlorate. This behavior is due to the complexing action of these ions, which becomes more pronounced as the pH increases, since ionization of the corresponding ions is enhanced. CHOLAK *et al.*[6] extracted zinc from a 6% citrate solution using chloroform, and their $pH_{1/2}$ of 7.5 agrees roughly with our values if differences in concentration and phase volumes are considered. In the 0.001 *M* NTA extractions, indications are that the complexing agent predominates beyond a pH of about 5.0, overcoming the dithizone complex formation, and decreasing the extraction. With $0.01M$ NTA, complexing is active over the whole pH range, preventing the expected curve from being shown. The citrate ion in systems employing carbon tetrachloride or benzene as the non-aqueous phase had only a small effect, since the low pH values kept most of the citrate in the acid form. EDTA prevented extraction in all cases, which is not surprising in view of the great stability of the zinc–EDTA complex.

Non-aqueous solvent effects

The effects of changing the organic phase are summarized in Table II. Plots of log E against (log$[HR]$ + pH) for the extractions from $0.10M$ perchlorate systems with dithizone in the various solvents showed slope values of 1.8 for chloroform, 2.0 for benzene, 2.2 for chlorobenzene, and 2.2 for carbon tetrachloride. These values tend to confirm the 1 : 2 ratio for the zinc–dithizone complex. Eqn.(3) predicts that at the same value of E, the quantity $[H]^2S_r^2/S_c$ should be a constant regardless of the non-aqueous solvent. Calculations show that this is roughly so.

TABLE II

EFFECT OF NON-AQUEOUS SOLVENT ON EXTRACTION OF ZINC DITHIZONATE FROM AQUEOUS SOLUTION

Solvent	*K*	*Solubility (g/l)*[a]	
		HR	*ZnR*$_2$
Chloroform	$3 \cdot 10^{-2}$	20.3 ± 0.3	21.0 ± 0.8
Dichloromethane	$1 \cdot 10^{0}$	12.6 ± 0.5	16.4 ± 0.3
Benzene	$8 \cdot 10^{0}$	3.6 ± 0.1	2.3 ± 0.3
Chlorobenzene	$2 \cdot 10^{1}$	2.5 ± 0.1	4.6 ± 0.3
Carbon Tetrachloride	$5 \cdot 10^{1}$	0.74 ± 0.02	0.72 ± 0.06

[a] The solubility values are averages of six determinations. Standard deviations are attached.

Spectral studies

Absorption spectra of dithizone and zinc–dithizonate in various solvents have been reported in the literature[6,7]. In this study spectra of these compounds were determined in several other solvents. The spectra of dithizone were determined in carbon disulfide, chlorobenzene, dichloromethane, and nitrobenzene. No significant changes in the positions of the absorption maxima (450 and 600 millimicrons) were noted. Some differences in hue were found, this being due to varying heights of the maxima. Contrary to literature reports[7], nitrobenzene and nitromethane solutions of dithizone are not yellow, although they will become so upon standing, this change being due to slow oxidation of the solute. Absorption spectra of zinc–dithizone in benzene, chlorobenzene, and dichloromethane showed no major changes in the curves.

EXPERIMENTAL CONDITIONS

Chemicals

All solutions were prepared with distilled and demineralized water. All chemicals were of U.S.P. grade or better. Salts were purified of heavy-metal contaminants by preliminary extractions with chloroform solutions of dithizone. Solvents were purified and recovered by procedures similar to

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that of Biddle[8]. Eastman reagent grade dithizone was repurified by the procedure given by Welcher[9]. Zinc dithizonate was prepared in the manner of Wasserman and Suprunovich[10], followed by recrystallization from chloroform.

Apparatus

All measurements of pH were made with a Beckman Model H pH Meter. The absorption spectra were measured with a Beckman Model DU Spectrophotometer. All other optical density measurements were made on a Bausch and Lomb Spectronic Model 20 Spectrophotometer. Samples were stirred by a battery of magnetic stirrers mounted under a shallow bath which controlled the temperature at 30.0 ± 0.5°.

The technique

Zinc solutions were prepared by dissolving weighed samples of zinc carbonate in perchloric acid and dilution to the desired concentration. Any anions desired in the aqueous phase were supplied in the form of sodium salts. All aqueous solutions were brought to an ionic strength of 0.10 by the addition of sodium perchlorate.

Twelve samples, including one blank, were run in parallel during each determination. For each sample, 10.00 ml of properly prepared zinc solution ($10^{-5}M$) was adjusted to a predetermined pH value by the addition of perchloric acid and/or sodium hydroxide solution. The samples were then transferred to 25-ml glass-stoppered Erlenmeyer flasks, and exactly 5.00 ml of dithizone solution ($1.8 \cdot 10^{-3}M$) was added to each, after which they were stirred for 8 h at 30°. At the end of this period, a 1.00-ml aliquot of the non-aqueous phase was removed from each sample, diluted with 10.00 ml of solvent, and analyzed spectrophotometrically for zinc. In addition, the pH value of each aqueous phase was again measured.

Solubilities of dithizone and zinc dithizonate were determined at 30° in several solvents. Equilibration was achieved by stirring for approximately 15 h, three of six samples being cooled to the final temperature, and the others being warmed to it. Aliquots were withdrawn through a filter-paper cone, diluted quantitatively, and analyzed spectrophotometrically.

Absorption spectra of dithizone and zinc dithizonate in the range of 350–700 millimicrons were determined in several solvents. All solutions used in these measurements had a solute concentration of about $10^{-5}M$.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to The Southern Fellowship Fund for a financial grant and to Tennessee Wesleyan College for a grant of time, both of which were indispensable for the pursuit of this problem.

SUMMARY

The extraction of $10^{-5}M$ zinc ion from aqueous solution into an organic solvent $1.8 \cdot 10^{-3}M$ in dithizone has been investigated. The effects of pH, other ions in the aqueous phase including ions which complex with zinc, and various organic solvents have been investigated. Ions which complex with zinc (citrate, oxalate, nitrilotriacetate, ethylenediaminetetracetate) change the position and/or shape of the extraction curve. Changes in the organic solvent alter the position of the curve, this alteration being qualitatively related to the solubility of dithizone in the organic solvent. Spectra for dithizone and for zinc dithizonate in several organic solvents have also been determined.

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Received January 8th, 1958

THE CHEMICAL ANALYSIS OF TERNARY ALLOYS OF PLUTONIUM WITH MOLYBDENUM AND URANIUM

by

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INTRODUCTION

Methods for the chemical analysis of alloys of plutonium and uranium[1,2], of molybdenum and uranium[3], and of molybdenum, uranium and niobium[4,5], have been published, but these methods would be unsatisfactory if applied to ternary alloys of plutonium, uranium and molybdenum. In particular, the absorptiometric determination of uranium as uranyl sulphate in 4N sulphuric acid at 4300 Å[5] would suffer interference from plutonium-III, -IV and -VI sulphates. The absorptiometric determination of plutonium as plutonium-III at 5650 Å might be satisfactory in the presence of molybdenum provided that the solutions do not form a coloured molybdenum compound on adding a reducing agent. The absorptiometric determination of molybdenum itself by means of the intense thiocyanate colour at 5000 Å should be satisfactory in the presence of uranium and of plutonium.

EXPERIMENTAL

Dissolving the ternary alloy

We examined alloys over the range 14.7% w/w Mo, 0–85.3% Pu, 85.3–0% U. The ternary alloys were found to dissolve on treatment with 6N HCl, then mixed HCl–HNO_3, with a little HF for alloys containing more than 50% of plutonium. Binary alloys of plutonium and uranium would give clear solutions after this treatment: the presence of molybdenum necessitates the additional step of fuming with sulphuric acid in order to bring about complete solution. Perchloric acid may be substituted for sulphuric acid in this step, provided care is taken not to boil off all the nitric acid; if the fuming is prolonged to this extent, then a molybdenum compound is precipitated. The use of sulphuric acid is essential on any portion of the solution which will subsequently be used for the determination of molybdenum as thiocyanate.

Determination of molybdenum

Solutions containing molybdenum, mixtures of molybdenum with uranium and of molybdenum with plutonium, all in sulphuric acid solution, were treated under standard conditions[4] to produce the molybdenum thiocyanate colour. The absorption spectra were examined using a Unicam spectrophotometer and showed that uranium (up to 250/1) and plutonium (up to 15/1) would not contribute to the measured absorbancy at 5000 Å. A further series of mixtures (to cover the expected range of alloy compositions) were treated with thiocyanate reagent and measured on the Spekker, using a mercury vapour lamp and an Ilford 603 filter to isolate the 4916Å line. The results (Table I) were satisfactory.

TABLE I

ABSORPTIOMETRIC DETERMINATION OF MOLYBDENUM AS THIOCYANATE IN THE PRESENCE OF URANIUM AND PLUTONIUM

Weight Ratio U/Mo	*Weight Ratio Pu/Mo*	*Absorbancy (against water)*
0	0	0.488
0.1	5.5	0.488
0.5	5.0	0.494
1.5	2.5	0.490
2.5	1.5	0.487
5.0	0.5	0.487
5.5	0.1	0.492

The determination of molybdenum as thiocyanate is made erratic by any nitrate ion remaining in solution following the dissolving of the alloys and the aliquot taken for this determination must be fumed with sulphuric acid to remove all nitrate

Attempted absorptiometric determination of plutonium in the presence of molybdenum

In preliminary experiments, we prepared mixed solutions of plutonium and molybdenum in $3N$ sulphuric acid, the plutonium being initially partly in the Pu-IV and partly in the Pu-VI state.

We attempted to measure the intensity of the Pu-III colour after reduction with stannous chloride or ferrous sulphate, hydroxylamine being ineffective in the presence of sulphate, which strongly complexes Pu-IV.

The plutonium-III solutions were measured against water at 5780Å using a Spekker photoelectric absorptiometer with a mercury vapour lamp and Ilford 606 filters. High results were obtained when molybdenum was present (Table II).

TABLE II

THE ABSORBANCY OF PLUTONIUM SOLUTIONS, REDUCED IN THE PRESENCE OF MOLYBDENUM

Weight Ratios		*Reducing Agent*	*Absorbance*		*% Error*
Mo/Pu	*U/Pu*		*expected*	*found*	
1.0	4.7	$SnCl_2$ at 80°	0.387	0.505	+30.5
1.2	3.3	$FeSO_4$ at room temperature	0.372	0.414	+10.2
1.2[a]	0	,,	0	0.045	
0	3.3[a]	,,	0	0.005	

[a] Blank determinations in the absence of plutonium.

The weakly coloured solutions of molybdenum reduced with $FeSO_4$, showed a very broad absorption spectrum (examined on a Unicam spectrophotometer) and so the positive interference of molybdenum in this method of determination of plutonium cannot be avoided by an alternative choice of filters. It may be possible to determine

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plutonium as Pu-III, using hydroxylamine as reductant, in the presence of molybdenum if the solution contains no sulphate. We did not however examine this possibility.

Solvent extraction of molybdenum α-benzoin oxime

JONES[6] has shown that μg amounts of molybdenum are completely extracted from dilute sulphuric acid into chloroform in the presence of α-benzoin oxime: a solution of the reagent in alcohol is added to the aqueous sample and the precipitate is extracted into chloroform. We investigated the recovery of 30 mg molybdenum from dilute sulphuric and from dilute perchloric acid, and showed that plutonium and uranium (100 mg each) did not interfere (Table III). The synthetic mixture was compounded from individual solutions prepared by attacking U, Pu and Mo metals respectively with mixed HCl–HNO_3 followed by fuming with either H_2SO_4 or $HClO_4$. The Mo metal had been irradiated in BEPO to produce Mo-99 tracer, which was used to detect (by γ counting) any small amounts of molybdenum remaining in the aqueous phase. Any small loss of plutonium or of uranium with the molybdenum in the organic phase was detected by α counting (for plutonium) and fluorimetry (for uranium) respectively.

TABLE III

EFFICIENCY OF SEPARATION OF MOLYBDENUM FROM PLUTONIUM AND URANIUM

Acid	*Strength (N)*	*Extraction conditions*	*Aqueous phases*	*Chloroform phase*	
			% Mo left	*% Pu extracted*	*% U extracted*
H_2SO_4	0.3	A	< 0.1	0.6	0.25
	0.6	A	< 0.1	0.15	0.15
	1.5	A	0.2	0.1	0.08
	1.5	A	0.4	—	—
	2.5	A	~ 40	0.1	0.2
$HClO_4$	0.1	A	4.3	—	—
	0.7	A	2.4	—	—
	1.3	A	2.0	—	—
	1.9	A	2.0	—	—
	2.4	A	4.3	—	—
	3.0	A	8.5	—	—
	1.5	B	0.2	0.28	0.04
	1.5	B	0.1	0.07	0.02

Extraction conditions A consisted of adding 25 ml of 2% α-benzoin oxime in alcohol to 25 ml of aqueous sample, shaking, and extracting three times with successive 15-ml portions of chloroform.

The combined chloroform extract is washed once with dilute acid of the same strength as the aqueous sample.

Extraction conditions B included one extra precipitation with α-benzoin oxime, using the aqueous residue from the first stage. Each precipitate was extracted with three successive portions of chloroform, and the combined extracts were washed with dilute acid. The compound of molybdenum and α-benzoin oxime does not seem to be completely soluble in the chloroform, but gives a milky suspension. The procedure is nevertheless effective in removing molybdenum without significant loss of plutonium.

Separation of plutonium from uranium

The molybdenum having been removed, the plutonium and uranium could in principle be separated quantitatively using the anion exchange method[4]. This separation has been applied only to solutions containing hydrochloric and nitric acids. It gave low uranium recoveries (e.g. 90%) when applied to solutions containing sulphate [illegible]duced in the initial dissolving of the ternary alloys. Attempts to reduce the [illegible] of residual sulphate by evaporation and prolonged fuming of the solutions [illegible] the solvent extraction of molybdenum were not entirely successful. Satisfactory results were achieved by excluding sulphate from the solutions: with care the ternary alloys were completely dissolved by treatment with HCl, HNO_3 and HF, followed by fuming with $HClO_4$. (The fuming was not so prolonged as to remove all the perchloric acid). The presence of $HClO_4$ did not prevent the removal of molybdenum as [illegible] (see Table II) nor the subsequent separation of plutonium and uranium in 7 N HNO_3, the perchloric acid concentration at this stage being < 5 N. The latter point is illustrated by the analytical results on synthetic mixtures given below.

TABLE IV

RECOVERY OF PLUTONIUM FROM ANION EXCHANGE [illegible]

Pu taken mg	Experiment	Pu found in U fraction mg	Pu [illegible]	Pu found in Pu fraction mg
28.8	A	0.024	[illegible]	28.7
28.8	B	0.029	[illegible]	28.6

Experiment A: absorption from 7 N HNO_3 + 3 N $HClO_4$, [illegible]ing with 60 ml 7 N HNO_3, elution with 25 ml 10% $NH_2OH \cdot HCl$.
Experiment B: absorption from 7 N HNO_3, washing with [illegible] ml 7 N HNO_3, elution with 25 ml 10% $NH_2OH \cdot HCl$.

No uranium was present in experiments A and B.

TABLE V

RECOVERY OF URANIUM FROM URANIUM–PLUTONIUM MIXTURES

U taken mg	Pu taken mg	U found mg
[illegible]	28.8	[illegible]
[illegible]	28.8	[illegible]

METHOD

Dissolving the alloy

Details of health precautions taken during analytical sampling and dissolving [illegible] plutonium alloys alloys are included in an earlier paper[3].

The weight of alloy taken should preferably contain at least 150 mg [illegible] 20 mg uranium and 10 mg molybdenum, to permit duplicate determinations by the methods described below. The weighed sample is treated with 20 ml of 6 N HCl and allowed to [illegible] until any reaction subsides; then 20 ml of concentrated HNO_3 are added, with gentle warming [illegible] an hour. 5 ml of concentrated $HClO_4$ are now added and the mixture warmed for an hour. [illegible] solution is not complete at this stage, 0.1 ml of concentrated HF solution is added and the [illegible] is warmed for a further hour and finally heated strongly to boil off HCl, HF and the bulk [illegible] HNO_3. Heating should not be prolonged to the extent that dense fumes of $HClO_4$ are evolved over a long period, otherwise a precipitate of molybdic oxide may appear. The solution is diluted to about 30 ml. Any persistent insoluble material is filtered off and weighed as described previously[1]. The filtered solution is made up accurately to 50 ml.

Molybdenum determination

5.00 ml of the solution of the sample are fumed strongly with 10 ml of concentrated H_2SO_4 to remove all nitric acid; the mixture is cooled and carefully diluted to 25.0 ml. 5.00-ml aliquots are taken (in duplicate), added to a flask, followed by 20 ml of 6.4N H_2SO_4, 5 ml of 0.2M $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, 1 ml of perchloric acid (sp. gr. 1.54), 5 ml of 1.5M NH_4CNS and 5 ml of 0.5M $SnCl_2$, and the mixture is made up to 50.0 ml with water. The absorbancy of the molybdenum thiocyanate colour is determined differentially against a standard of comparable intensity prepared from pure molybdenum metal. The coloured solutions are allowed to stand for 10 min before measurement and they are compared at the same temperature. The differential comparison may be made using the Spekker with the mercury lamp and Ilford [illegible] filters or a spectrophotometer (*e.g.* the Uvispek at 5000 Å) using a slit width of 0.06 mm).

Removal of molybdenum before the determination of plutonium and uranium

20.0 ml (in duplicate) of the solution of the sample in $HClO_4$ (plus residual HNO_3) are added to a separating funnel. The solution should be at least 1.5N in total acid at this point (maximum permissible range 1.5–2.0N); 10 ml of a 2% solution of α-benzoin oxime in EtOH are added, and the precipitate is extracted three times with 10-ml portions of $CHCl_3$. The molybdenum α-benzoin oxime compound forms a milky suspension in the $CHCl_3$ phase and is removed. The last traces of molybdenum are removed by adding a further 10 ml of 2% α-benzoin oxime, followed by three extractions each with 10-ml portions of $CHCl_3$. The combined molybdenum extracts are washed

TABLE VI

RESULTS

(a) Synthetic mixtures [illegible]		% Composition by weight			Total % recovery
		Mo	*Pu*	*U*	
A	Taken	19.8	29.4	50.8	
	Found	19.9	29.4	50.4	99.7
B	Taken	18.5	60.6	20.9	
	Found	18.4	60.0	20.6	99.0
C	Taken	12.5	9.1	78.4	
	Found	12.8	9.2	78.2	100.2
D	Taken	11.9	81.1	7.0	
	Found	11.8	81.5	7.0	100.3

(b) Alloy samples [illegible]		% Composition by weight			Total % recovery
		Mo	*Pu*	*U*	
E1	Nominal	14.7	0.0	85.3	100.0
	Found	14.7	0.1	85.0	99.8
E2	Nominal	14.7	21.3	64.0	100.0
	Found	15.8	21.0	63.6	100.4
E3	Nominal	14.7	42.6	42.6	100.0
	Found	13.2	45.2	42.0	100.4
E4	Nominal	14.7	64.0	21.3	100.0
	Found	13.0	66.0	22.0	101.0
E5	Nominal	14.7	85.3	0.0	100.0
	Found	12.5	87.5	0.1	100.1

twice with 10-ml portions of 1.5*N* $HClO_4$, which are added to the residual aqueous solution. The combined aqueous solutions, containing all the uranium and the plutonium, are boiled to remove EtOH, cooled and prepared for addition to an anion exchange resin and the subsequent separation and determinations of uranium and plutonium is carried out, as previously reported[1]. If required, the plutonium may be determined in the presence of the uranium[2], up to at least a ratio U/Pu = 8.

SUMMARY

It is shown that the absorptiometric determination of molybdenum as thiocyanate may be used in the presence of plutonium. Molybdenum interferes with previously published methods for determining uranium and plutonium but conditions have been established for its complete removal by solvent extraction of the compound with α-benzoin oxime. The previous methods for uranium and plutonium are satisfactory when applied to the residual aqueous phase following this solvent extraction.

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Received January 6th, 1958

PRECIPITATION OF ZINC SULFIDE BY THE HYDROLYSIS OF THIOACETAMIDE

by

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The precipitation of zinc sulfide by hydrogen sulfide gas from a solution in which the pH is maintained between 2 and 3 serves to separate zinc from iron, manganese, aluminum, chromium, nickel, and cobalt. The separation from cobalt is not complete; a small amount of cobalt is always carried down on the zinc sulfide precipitate. The separation can be improved by adding ammonium thiocyanate which complexes the cobalt thus reducing coprecipitation. Various buffer mixtures have been recommended; these include formate–formic acid[1], sulfate–sulfuric acid[2], chloracetate–chloracetic acid[3], and citrate–citric acid[4].

Thioacetamide has been used in place of hydrogen sulfide to precipitate various sulfides. The use of thioacetamide was first suggested by Barber and Grzeskowiak[5]. Soon thereafter Flaschka and Jakobljevich[6] investigated the use of thioacetamide for the quantitative precipitation of antimony, bismuth, molybdenum, copper, arsenic, cadmium, lead, tin, and mercury. The precipitates obtained were coarser

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and less contaminated with foreign ions. They found that precipitated metal sulfides were frequently contaminated with free sulfur. Flaschka also reported that "Only a slight turbidity results from the boiling of neutral or weakly acidic solutions of thioacetamide and zinc salts"[7].

Swift and Butler[8] found that with hydrogen ion concentrations less than 0.02*M*, hydrolysis of thioacetamide required several hours and that subsequent hydrolysis of acetamide took place to a considerable extent. From the rate data obtained they predicted that at pH 2.7, a solution 0.01*M* in zinc salt and 0.1*M* in thioacetamide would require a time of 4.5 h for hydrolysis to produce a quantity of hydrogen sulfide equivalent to the zinc present. When this was tried experimentally, however, less than one milligram of zinc was recovered. Since hydrolysis proceeds more rapidly at higher temperatures the precipitation of zinc sulfide by the hydrolysis of thioacetamide under pressure was investigated.

In the following investigation the effect of temperature, pressure and concentration of reactants upon the time required for the complete precipitation of zinc sulfide by the hydrolysis of thioacetamide was studied. It was hoped that the coprecipitation of cobalt would be improved by the use of thioacetamide.

EXPERIMENTAL

Reagents

Thioacetamide. The reagent used was from Eastman Kodak Co. No. 1719. A 1*M* aqueous solution was prepared and filtered before using.

Zinc nitrate solution. Prepared by dissolving 45.4 g of the hexahydrate in 1 l of solution.

Diammonium hydrogen phosphate reagent. A little water was used to dissolve 107 g of the salt. The solution was neutralized with ammonium hydroxide to phenolphthalein, filtered, and diluted to one liter.

Diammonium tetrathiocyanatomercury(II) reagent. Prepared by dissolving 27.2 g of mercuric chloride and 33.6 g of ammonium thiocyanate in 1 l of solution.

Citrate–citric acid buffer. Prepared by adding ammonium hydroxide to 1*N* citric acid until pH 2.2 was obtained using a Beckman pH Meter (standardized using 0.01*M* $KH_3(C_2O_4)_2$ at pH 2.15).

Sulfate–bisulfate buffer. Prepared by dissolving 100 g sodium sulfate decahydrate in 900 ml of solution and 13 g sodium bisulfate monohydrate in 100 ml of solution. The bisulfate was added until pH 2 was obtained using the Beckman pH meter.

Ammonium thiocyanate. A 20% solution was used.

Standardization of zinc nitrate solution. Two methods were employed. Precipitations were made from 10-ml portions of the zinc solution using diammonium hydrogen phosphate[9] and diammonium tetrathiocyanatomercury(II)[10]. The precipitates were filtered on a medium-porosity sintered glass crucible, washed, then dried at 105° to 110° and weighed. The value found was 10.02 mg of zinc per ml.

PROCEDURES

Precipitation of zinc sulfide by the hydrolysis of thioacetamide in sealed tubes

A slight constriction was made in the top of a 13 × 17 × 300 mm pyrex combustion tube producing a funnel-like opening. With a pipet, 3 ml of standard zinc solution was transferred to the tube. This was washed into the tube using three 3-ml portions of citrate–citric acid buffer, two 3-ml portions of ammonium thiocyanate and 3 ml of 1*M* thioacetamide. This procedure was adapted from Coleman and Smith[4].

The tube was cooled in ice, the remaining air space warmed and the tube sealed. The tube was wrapped in glass wool, placed in an iron pipe with screw caps on each end and heated in a drying oven at a temperature of 120° for 2 h. The tubes were allowed to cool, scratched with a file and opened by applying a white hot glass rod to the moistened file mark. The zinc sulfide was transferred to a centrifuge tube using the clear supernate to wash the tube clean. The precipitate was washed with dilute ammonium nitrate solution and dissolved in hydrochloric acid. A few drops of nitric acid was added to coagulate the colloidal sulfur. Free sulfur was removed by centrifuging while transferring the solution to a beaker. Total volume after repeated washing of free sulfur and centrifuge tube was about 50 ml. Zinc was precipitated and weighed as $Zn[Hg(CNS)_4]$. This method was found more convenient than precipitation as $ZnNH_4PO_4$. The results are summarized in Table I.

Precipitation of zinc sulfide by the hydrolysis of thioacetamide in pressure bottles

Pressure bottles (200 ml, obtained from E. H. Sargent and Co.) were used in the following procedure. The pressure bottles were filled using 3 ml of standard zinc solution, 30 ml of citrate–citric acid buffer, 20 ml ammonium thiocyanate and 5 ml of thioacetamide. Samples were precipitated also using 30 ml sulfate–bisulfate buffer as outlined by JEFFREYS AND SWIFT[2].

A sample containing 200 mg of zinc was completely precipitated in the presence of 20 ml of thioacetamide but not with 10 ml; intermediate amounts were not investigated. With 10-ml portions of standard zinc solution, 10 ml of thioacetamide was sufficient. The volume of the solution appears to be a significant factor in determining the quantity of thioacetamide required.

Before sealing the pressure bottle, the solution was boiled on a Glas-Col heating mantle for several minutes to expel air. The bottles were wrapped in a cloth, placed in a metal can and heated in a drying oven at a temperature of 120° for a period of 3 h. The bottles were allowed to cool at room temperature for at least 20 min to avoid loss on opening. The zinc sulfide was washed into centrifuge tubes using the supernate until the pressure bottles were clean. The precipitate was then treated as outlined above. The results are given in Table II.

Contamination of zinc sulfide obtained by the hydrolysis of thioacetamide in the presence of cobalt

The procedure used in the pressure bottles was repeated adding 10.3 mg of cobalt carrier and ^{60}Co tracer having an activity of 11,844 counts/min. The zinc sulfide was washed into centrifuge tubes using the supernate until the pressure bottles were clean. The resulting precipitate was washed twice with dilute ammonium nitrate and counted in a well-type scintillation counter. The results obtained are given in Table III.

TABLE I

PRECIPITATION OF ZINC SULFIDE BY HYDROLYSIS OF THIOACETAMIDE IN SEALED TUBES

Zn used mg	CH_3CSNH_2 ml	$Zn[Hg(CNS)_4]$ g	*Zn calculated* mg	*Difference* mg
30.06	3	0.2274	29.83	—0.23
30.06	3	0.2239	29.38	—0.68
30.06	3	0.2301	30.19	+0.13
30.06	3	0.2278	29.89	—0.17
30.06	9[a]	0.2248	29.49	—0.57
30.06	9[a]	0.2275	29.85	—0.21
100.20	10[a]	0.7514	99.90	—0.30

[a] No NH_4CNS added.

TABLE II

PRECIPITATION OF ZINC SULFIDE BY HYDROLYSIS OF THIOACETAMIDE IN PRESSURE BOTTLES

Zn used mg	CH_3CSNH_2 ml	*Total volume solution* ml	$Zn[Hg(CNS)_4]$ g	*Zn calculated* mg	*Difference* mg
		Citrate–citric acid buffer			
30.06	5	88	0.2260	29.65	— 0.41
30.06	5	58	0.2267	29.74	— 0.32
30.06	10	63	0.2301	30.19	+ 0.13
100.20	10	70	0.7652	100.39	+ 0.19
100.20	10	70	0.7649	100.35	+ 0.15
		Sulfate–bisulfate buffer			
30.06	5	58	0.2306	30.25	+ 0.19
30.06	10	63	0.2267	29.74	— 0.32
100.20	10	70	0.7683	100.80	+ 0.60
100.20	10	70	0.7673	100.67	+ 0.47
100.20	10	70	0.7700	101.02	+ 0.82
200.40	20	90	1.5303	200.78	+ 0.38

TABLE III

DETERMINATION OF COBALT CONTAMINATION OF ZINC SULFIDE USING THIOACETAMIDE

Zn used mg	*CH_3CSNH_2 ml*	*Time h*	*Total volume solution ml*	*Activity[c] carried on ZnS c.p.m.*	*Wt. of Co[c] coprecipitated mg*	*% of Cobalt coprecipitated*
			Citrate–citric acid buffer			
30.06	3[b]	2	22	186	0.16	1.57
30.06	3	2	22	175	0.15	1.47
30.06	5	2	93	145	0.13	1.22
30.06	5	2	93	205	0.18	1.73
100.20	10	2	71	214	0.19	1.81
100.20	10	2	71	1990	1.73	16.80
30.06	10	3	64	1507	1.31	12.72
30.06	10	3	64	1793	1.56	15.14
			Sulfate–bisulfate buffer			
30.06	5	2.5	59	198	0.17	1.67
30.06	5	2.5	59	337	0.29	2.85
30.06	10[a]	3	64	2674	2.33	22.58
30.06	10[a]	3	64	2418	2.10	20.42
100.20	10	3	71	3352	2.91	28.30
100.20	10	3	71	2207	1.92	18.63

[a] No NH_4CNS added

[b] Sealed tube

[c] 10.3 mg of Co(II) carrier, and 11,844 c.p.m. of ^{60}Co tracer was added to each sample.

TABLE IV

DETERMINATION OF COBALT CONTAMINATION OF ZINC SULFIDE USING HYDROGEN SULFIDE

Zn used mg	*Total volume solution ml*	*Time h*	*Activity[b] carried on ZnS c.p.m.*	*Wt. of Co[b] coprecipitated mg*	*% of Cobalt coprecipitated*
			Citrate–citric acid buffer		
30.06	22	1	245	0.21	2.07
30.06	22	1	558	0.48	4.71
30.06	54	1	38	0.03	0.32
30.06	54	3	32	0.03	0.27
30.06	54	2	36	0.03	0.30
100.20	61	4	31	0.03	0.26
100.20	61	3	43	0.04	0.36
100.20	61	2	29	0.03	0.25
			Sulfate–bisulfate buffer		
30.06	54[a]	1	58	0.05	0.49
30.06	54[a]	1	62	0.05	0.52
30.06	54	2	25	0.02	0.21
30.06	54	1	24	0.02	0.20
30.06	54	3	16	0.01	0.14
100.20	61	2.5	—	—	—
100.20	61	2	—	—	—
100.20	61	1	13	0.01	0.11

[a] No NH_4CNS added

[b] 10.3 mg of Co(II) carrier and 11,844 c.p.m. of ^{60}Co tracer was added to each sample.

Contamination of zinc sulfide obtained by precipitation with hydrogen sulfide gas in the presence of cobalt

The above procedure was followed except that hydrogen sulfide gas was substituted for thioacetamide and the reaction was carried out in 125-ml Erlenmeyer flasks. The solution was warmed, the air replaced by hydrogen sulfide, heated nearly to boiling and zinc sulfide precipitated using hydrogen sulfide gas at a pressure of two atmospheres. Precipitation was complete in 30 min with 30-mg samples and in 5 min with 100-mg samples. The precipitates were allowed to stand for varying periods of time before centrifuging, washing and counting. The results obtained are given in Table IV.

CONCLUSION

It was hoped that a precipitate obtained by the hydrolysis of thioacetamide might be less contaminated by foreign ions. The precipitate obtained was coarse and easily centrifuged but carried more cobalt contamination than that produced with hydrogen sulfide. This was probably caused by a direct reaction between cobalt and thioacetamide resulting in the direct precipitation of some cobalt sulfide. Swift *et al.* observed a similar phenomenon in their study of the precipitation of nickel with thioacetamide[11]. Best separations were obtained using a sulfate–bisulfate buffer containing ammonium thiocyanate with hydrogen sulfide as a precipitant.

ACKNOWLEDGEMENT

The authors wish to thank the National Science Foundation for the grant which made this research possible.

SUMMARY

Zinc can be precipitated quantitatively as zinc sulfide using thioacetamide in a weakly acid solution. This is accomplished by carrying out the reaction in a sealed tube at 120°. The method, however, does not give a good separation from cobalt. Best separations are obtained by using a sulfate–bisulfate buffer containing ammonium thiocyanate with hydrogen sulfide as precipitant.

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Received January 17th, 1958

THE DETERMINATION OF FLUORINE IN RARE EARTH FLUORIDES BY HIGH TEMPERATURE HYDROLYSIS*

by

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INTRODUCTION

The preparation of pure rare earth metal is often accomplished by the reduction of the corresponding rare earth fluoride. These fluorides are generally prepared by the high temperature hydrofluorination of the rare earth oxides. The latter procedure necessitates a rapid and accurate method for the analysis of rare earth fluorides to indicate whether the oxide has been completely converted to the fluoride.

PRIDEAUX AND ROPER[1] analyzed fluorides of zirconium and potassium hydrogen fluoride by passing steam over the sample contained in a platinum tube which was held at a bright red heat. The hydrofluoric acid formed was titrated with standard alkali. WARF, CLINE, AND TEVEBAUGH[2] recognized the potential of this technique and extended it to the analysis of many metal halides. They coined the word "pyrohydrolysis" to describe this method.

WARF *et al.* divided the fluorides into two groups, a rapidly hydrolyzable and a slowly hydrolyzable group. The former included the fluorides of aluminum, bismuth, magnesium, thorium, uranium, zinc and the rare earths. The second group included the fluorides of the alkali metals, the alkaline earth metals, and beryllium. The fluorides in the first group were reported to be hydrolyzed quantitatively in 20 min or less at 1000°, whereas the fluorides in the second catagory were slowly hydrolyzed. No data were given which justified the classification of rare earth fluorides as readily hydrolyzable substances. However, in an earlier report[3], data were given which would seem to be the basis for their classification. In this earlier work it was reported that the pyrohydrolysis of cerium fluoride required 10 min and results were high, dysprosium fluoride required 26 min and results were high, and gadolinium fluoride required 40 min. Lanthanum, neodymium, and samarium fluorides were pyrohydrolyzed and the percentage fluorine was reported to be nearly equal to the theoretical value, except for lanthanum fluoride which was quite low. No data were given which indicated the time required for complete pyrohydrolysis of these three fluorides. WARF AND CLINE[3] suggested that their data indicated that the original oxide was impure or that perhaps the oxides were incompletely hydrofluorinated.

It was reported that light metal fluorides were pyrohydrolyzed in a relatively short time in the presence of air when mixed with an accelerator, U_3O_8. Several other oxides were studied which acted as pyrohydrolytic accelerators. Aluminum oxide was reported to increase the rate of pyrohydrolysis of calcium and sodium fluorides, although it was less effective than U_3O_8. Chromium(III) oxide was comparable to the latter but its use gave results which were low and showed poor precision. They reported vanadium(V) oxide to be a good accelerator but it usually caused high results.

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* Contribution No. 576. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

The possibility of using the pyrohydrolysis technique for the analysis of the rare earth fluorides seemed attractive since almost all other methods were more time consuming[4-7] or only useful for the determination of smaller amounts of fluorine[8-10]. Accordingly, an investigation of the rate of pyrohydrolysis of pure rare earth fluorides at approximately 1000° was undertaken.

Data are presented which indicate that it is not possible to pyrohydrolyze all the rare earth fluorides quantitatively in 20 min or less at 1000°. The more basic rare earths require, in general, considerably longer pyrohydrolysis times. Chromium(III) oxide and uranium oxide, U_3O_8, were found to be useful accelerators for the pyrohydrolysis of these fluorides.

APPARATUS AND REAGENTS

Pyrohydrolysis apparatus, macro scale

The apparatus used was the same as that described by WARF *et al.*[2]. SUSANO, WHITE AND LEE[11] have described a less expensive apparatus for the pyrohydrolytic determination of fluorine which was constructed of nickel and stainless steel rather than platinum and silica.

Dempsy furnace

A high temperature hydrofluorination furnace was used to dry the rare earth fluorides.

Uranium oxide, U_3O_8

The accelerator was prepared by ignition of uranium(VI) nitrate 6-hydrate at 1000° for two hours[12].

Chromium(III) oxide, Cr_2O_3

The accelerator was prepared by ignition of chromium(VI) oxide at 1000° for 2 h to chromium(III) oxide[13,14].

Rare earth fluorides

Scandium, yttrium, lanthanum, cerium(III), praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium fluorides were prepared by dissolving the appropriate rare earth oxide in hot hydrochloric acid, transferring to a platinum dish, and precipitating as the fluoride by the addition of an excess of hot 48% hydrofluoric acid. In the case of cerium(IV) oxide some hydrogen peroxide was added in the dissolution process. The precipitated fluoride was digested for 30 min, cooled, separated by centrifugation, washed, and dried over anhydrous magnesium perchlorate in a vacuum desiccator. The fluoride was then ground, transferred to a small Monel tray and placed in a Dempsy high-temperature furnace. A continuous flow of anhydrous hydrofluoric acid was passed through the furnace and the temperature was raised to 600° over a period of 4 h and maintained at this value for another 4 h. The resulting anhydrous fluorides were allowed to cool to room temperature in the furnace in an atmosphere of anhydrous hydrofluoric acid and then stored in a desiccator over anhydrous magnesium perchlorate.

Hydrogen peroxide

30% H_2O_2, reagent grade.

Hydrofluoric acid

48% HF, reagent grade.

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EXPERIMENTAL WORK

Rates of hydrolysis of rare earth fluorides

The macro pyrohydrolysis apparatus was adapted so that the condensate could be continuously titrated with standard sodium hydroxide solution delivered from a buret removed from the heat of the furnace. A magnetic stirrer was used so that the condensate would be continuously stirred. Samples of various rare earth fluorides were pyrohydrolyzed at 975 ± 25° and the evolution of hydrogen fluoride followed as a function of time. The rates of hydrolysis for some of the rare earth fluorides are shown in Fig. 1. Table I shows the time required for complete hydrolysis of the rare earth fluorides, the percentage fluorine and rare earth metal found experimentally and the theoretical values.

Examination of these data shows that it is impossible to classify the rare earth fluorides as either rapidly or slowly hydrolyzable. The lighter rare earth and yttrium fluorides, but not

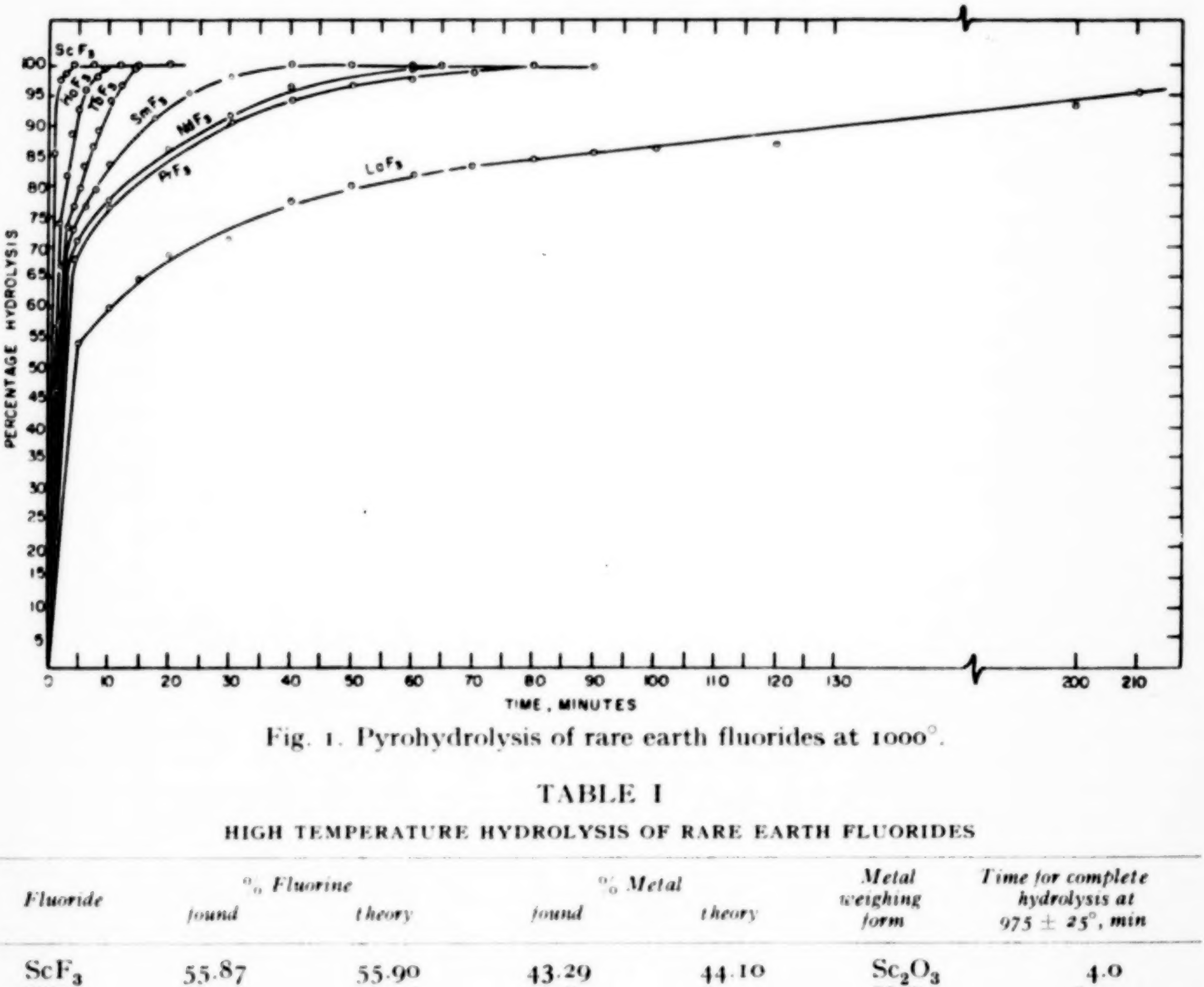

Fig. 1. Pyrohydrolysis of rare earth fluorides at 1000°.

TABLE I

HIGH TEMPERATURE HYDROLYSIS OF RARE EARTH FLUORIDES

Fluoride	*% Fluorine*		*% Metal*		*Metal weighing form*	*Time for complete hydrolysis at 975 ± 25°, min*
	found	*theory*	*found*	*theory*		
ScF_3	55.87	55.90	43.29	44.10	Sc_2O_3	4.0
YF_3	39.06	39.06	60.85	60.94	Y_2O_3	65.0
LaF_3	29.09	29.09	70.85	70.91	La_2O_3	250.0
CeF_3	28.80	28.91	70.99	71.09	CeO_2	5.0
PrF_3	28.79	28.80	71.18	71.20	Pr_6O_{11}	80.0
NdF_3	28.29	28.32	71.61	71.68	Nd_2O_3	65.0
SmF_3	27.50	27.48	72.42	72.52	Sm_2O_3	45.0
EuF_3	27.28	27.27	72.85	72.73	Eu_2O_3	70.0
GdF_3	26.64	26.65	73.06	73.35	Gd_2O_3	20.0
TbF_3	26.34	26.36	72.03	73.64	Tb_4O_7	14.0
DyF_3	25.96	25.97	74.11	74.03	Dy_2O_3	30.0
HoF_3	25.67	26.68	74.39	74.32	Ho_2O_3	12.0
ErF_3	25.41	25.42	74.63	74.58	Er_2O_3	22.0
TmF_3	25.18	25.18	74.87	74.82	Tm_2O_3	18.0
YbF_3	25.00	24.78	75.23	75.22	Yb_2O_3	7.0
LuF_3	24.56	24.57	75.30	75.42	Lu_2O_3	4.0

cerium fluoride, are difficult to hydrolyze completely, whereas the fluorides of the heavier rare earths, cerium and scandium are easily hydrolyzed.

The rare earth fluorides can be arbitrarily divided into two groups. Those of atomic number 64 and higher as well as cerium(III) and scandium can be pyrohydrolyzed in 30 min or less. Those of atomic number less than 64 and yttrium require from 45 to 150 min for complete hydrolysis.

The longer time required for the pyrohydrolysis of the latter group of rare earth fluorides makes the technique less useful. WARF *et al.*[2] overcame this difficulty in the case of the slowly pyrohydrolyzable alkali metal fluorides by using accelerators such as U_3O_8. The effect of U_3O_8 and other metal oxides on the rate of hydrolysis of the more difficultly pyrohydrolyzed rare earth fluorides was therefore studied.

TABLE II

EFFECT OF ACCELERATORS ON RARE EARTH FLUORIDES WHICH ARE DIFFICULT TO HYDROLYZE

Fluoride	*Accelerator*	*Time for complete hydrolysis at 975 ± 25°, min*	*% Fluorine*	
			found	*theory*
YF_3	—	65.0	39.06	39.06
YF_3	V_2O_5	30.0	39.45	39.06
YF_3	U_3O_8	10.0	39.08	39.06
YF_3	Cr_2O_3	16.0	38.87	39.06
YF_3	CeO_2	10.0	39.04	39.06
LaF_3	—	250.0	29.09	29.09
LaF_3	U_3O_8	90.0	29.06	29.09
LaF_3	Cr_2O_3	60.0	20.08	29.09
PrF_3	—	80.0	28.79	28.80
PrF_3	U_3O_8	65.0	28.82	28.80
PrF_3	Cr_2O_3	80.0	28.82	28.80
PrF_3	Cr_2O_3/U_3O_8[a]	40.0	28.77	28.80
NdF_3	—	65.0	28.29	28.32
NdF_3	U_3O_8	65.0	28.28	28.32
NdF_3	Cr_2O_3	65.0	28.27	28.32
NdF_3	Cr_2O_3/U_3O_8	45.0	28.32	28.32
SmF_3	—	45.0	27.50	27.48
SmF_3	U_3O_8	25.0	27.46	27.48
SmF_3	Cr_2O_3	45.0	27.54	27.48
EuF_3	—	70.0	27.28	27.27
EuF_3	U_3O_8	25.0	27.25	27.27
EuF_3	Cr_2O_3	35.0	27.27	27.27

[a] Mix Cr_2O_3 with the fluoride, then mix U_3O_8 with this mixture.

Table II shows the effect of various accelerators on the rare earth fluorides which are difficult to pyrohydrolyze. For instance the pyrohydrolysis of yttrium fluoride could be effectively accelerated with U_3O_8 in 10 min. Cerium(IV) oxide, chromium(III) oxide, and vanadium(V) oxide were also effective accelerators. High results were obtained when vanadium(V) oxide was used as an accelerator.

It is interesting to note at this point that, contrary to WARF AND CLINE's findings[3], vanadium (III) fluoride can not be pyrohydrolyzed at 1000° in 3 min since the fluoride sublimes at a temperature greater than 800° and is condensed in the receiving dish where it is subsequently titrated with sodium hydroxide, forming the black sodium vanadate. The formation of sodium vanadate near the end-point caused high results just as the accelerator, vanadium(V) oxide, caused high results for yttrium fluoride. The high results obtained when fluorine is determined in vanadium (III) fluoride were obviated by pyrohydrolysis of the sample at 700° for 10 min. Results obtained at this temperature are accurate and the precision is within two parts per thousand.

Uranium oxide, U_3O_8, was the most effective accelerator tested for yttrium, samarium, and europium fluorides and chromium(III) oxide the most effective accelerator for lanthanum. Neodymium and praseodymium fluorides were most effectively pyrohydrolyzed by a mixture of chromium(III) oxide and U_3O_8.

Procedure for the determination of fluorine in rare earth fluorides

The procedure used was the macro-scale procedure described by WARF, CLINE AND TEVEBAUGH[2]. If the fluoride is easily pyrohydrolyzed at 975 ± 25°, Table I gives the time required for complete pyrohydrolysis. After pyrohydrolysis the hydrofluoric acid is titrated with a standard solution of sodium hydroxide and the percentage of fluorine calculated. The percentage metal can be determined by weighing the rare earth oxide which results after pyrohydrolysis of the fluoride. The weighing forms of these oxides are given in Table I.

A fluoride which is in the category that is difficult to pyrohydrolyze, is subjected to pyrohydrolysis after mixing with the proper accelerator. The exact amount of accelerator is not critical as long as the weight ratio of fluoride to accelerator is at least one to ten. In order to make efficient use of the accelerator, the sample must be ground and mixed thoroughly with the accelerator. A micro mortar was used successfully for this process. After complete grinding, the accelerator–rare earth fluoride mixture is transferred to a platinum boat and pyrohydrolyzed. Table II lists the accelerator with the time required for complete pyrohydrolysis. The percentage fluorine is calculated after titration of the hydrofluoric acid with sodium hydroxide.

DISCUSSION

The high temperature hydrolysis data show that it is possible to determine fluorine in the rare earth fluorides accurately and in several cases rapidly. However, lanthanum and the more basic rare earths require excessive time for complete hydrolysis and necessitate the use of an accelerator such as U_3O_8 and/or Cr_2O_3. The use of an accelerator decreases the pyrohydrolysis time by at least 50%. The precision obtained when accelerators are used is comparable with unaccelerated pyrohydrolysis of a rapidly pyrohydrolyzable fluoride.

It is interesting to relate the ease of pyrohydrolysis to the basicity of the rare earths. Lanthanum is generally regarded as being the most basic and scandium the least, with the cerium family (La, Ce, Pr, Nd, Sm) being more basic than the yttrium family (Dy, Ho, Er, Tm, Y, Yb, La). This arrangement is supported by their order of precipitation with ammonia and also by their ease of pyrohydrolysis, cerium(III) fluoride being an exception.

SUMMARY

The technique of pyrohydrolysis has been applied to the determination of fluorine in the fluorides of scandium, yttrium, and the lanthanons. These fluorides have been divided into two classes according to their rate of hydrolysis. Lutetium, ytterbium, cerium(III), scandium, gadolinium, terbium, dysprosium, holmium, erbium, and thulium fluorides can be hydrolyzed in 30 min or less. Yttrium, lanthanum, praseodymium, neodymium, samarium, and europium fluorides require from 45 to 150 min for complete hydrolysis. Accelerators, such as uranium oxide (U_3O_8), chromium(III) oxide, and a mixture of these oxides have been used successfully to reduce the time required for quantitative hydrolysis of the fluorides in the latter group. The use of the correct accelerator reduces the hydrolysis time to 30 min or less for all these fluorides except lanthanum, praseodymium and neodymium.

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Received January 24th, 1958

SEPARATIONS INVOLVING SULPHIDES

VI. SEPARATION OF ALKALINE EARTH METALS FROM SOME ELEMENTS THAT FORM SULPHIDES

by

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In an earlier publication[1] it was shown that $2N$ sodium sulphide reagent[2] can be successfully used in the quantitative separation of arsenic, antimony, selenium and mercury from barium. In this paper procedures are given for the separation of rhenium, platinum, gold, bismuth, palladium, lead, cadmium and mercury from alkaline earths, as well as for their estimation. The general method followed in the estimations was to precipitate the elements belonging to the first group as sulphides by the addition of sodium sulphide reagent followed by excess of acid and to estimate the alkaline earth in the filtrate by a suitable method.

EXPERIMENTAL

Separation of rhenium and platinum from barium

Measured volumes of standard solutions of potassium perrhenate[3] or platinic chloride[4] and barium chloride[5] were mixed, and treated with 55–70 ml of $2N$ sodium sulphide reagent followed by a large excess of $12N$ hydrochloric acid and 10–15 g of ammonium acetate (solid). The concentration of the acid was adjusted to about $6N$. The mixture was heated to boiling to decompose the thiosalt of rhenium or platinum completely, and then allowed to cool to room temperature. The precipitate of rhenium heptasulphide or platinic sulphide was filtered through a weighed sintered glass crucible (porosity 4), and washed thoroughly with water (the filtrate being kept for the estimation of barium), ethanol and ether successively. The precipitate of rhenium heptasulphide was dried in a vacuum desiccator for $^1/_2$ h and weighed. The precipitate of platinum sulphide was dried at 105° for 1 h and weighed.

The filtrate was boiled to remove hydrogen sulphide etc., the free acid neutralized with ammonia (sp.gr. 0.88), then diluted to 250 ml and barium determined as $BaSO_4$.

55–70 mg of barium could be separated from 20–30 mg of rhenium or 17–23 mg of platinum. The metals were recovered with an accuracy of

Ba: 0.0 to −0.3% and Re: 0.0 to −0.27%;
Ba: 0.0 to −0.27% and Pt: 0.0 to −0.4%.

Separation of gold from barium

Measured volumes of standard solutions of barium chloride and auric chloride[6] were mixed and the procedure given for the separation of platinum from barium was followed, but the thiosalt of gold was decomposed with $2N$ hydrochloric acid only and the final acidity adjusted to about $1N$. Gold was determined as Au_2S_3.

In the filtrate barium was determined as $BaSO_4$.

55–70 mg of barium could be separated from 17–25 mg of gold. The metals were recovered with an accuracy of

Ba: + 0.02 to −0.27% and Au: + 0.06 to 0.38%.

Separation of bismuth, palladium, lead or cadmium from barium

Standard solutions of bismuth chloride[7], palladium chloride[8], lead acetate[7], cadmium acetate[7] and barium chloride were used. Measured volumes of the solutions of two ions were mixed and ammonia solution added in slight excess (in the case of lead, after neutralizing the acid with ammonia solution solid ammonium acetate was added to dissolve the precipitated lead chloride). The mixture was treated with 20–30 ml of 2*N* sodium sulphide reagent followed by enough 6*N* acetic acid to give a final concentration of about 3*N*. The mixture was heated to boiling to precipitate completely the metals as sulphides. The precipitate of palladium or lead sulphide after washing with ethanol and ether was dried in vacuum and weighed. The precipitate of bismuth trisulphide was dried at 105° for 1 h and weighed. The precipitate of cadmium sulphide was washed with hot 3*N* acetic acid (to prevent peptization), then thoroughly with ethanol and ether successively, dried at 105° for 1 h and weighed.

In the filtrate barium was determined as $BaSO_4$.

55–70 mg of barium could be separated from 50–65 mg of bismuth, 25–42 mg of palladium, 55–75 mg of lead or 45–55 mg of cadmium. The metals were recovered with an accuracy of

Ba: 0.0 to −0.17% and Bi: 0.0 to −0.3%;
Ba: 0.0 to −0.23% and Pd: 0.0 to −0.23%;
Ba: 0.0 to −0.24% and Pb: 0.0 to −0.31%;
Ba: 0.0 to −0.24% and Cd: 0.0 to −0.4%.

Separation of rhenium or platinum from strontium, calcium or magnesium

Standard solutions of potassium perrhenate, platinic chloride, strontium chloride[9], calcium chloride[10] and magnesium chloride[11] were used. Measured volumes of the solutions of two ions were mixed and treated as described for the separation of rhenium from barium. Rhenium and platinum were determined as sulphides.

The filtrate was boiled to remove hydrogen sulphide etc., the free acid neutralized with ammonia (sp.gr. 0.88) and diluted to 250 ml.

Strontium was determined as $SrSO_4$.

Calcium was precipitated as calcium oxalate and determined as calcium oxalate monohydrate or calcium carbonate.

Magnesium was precipitated as magnesium ammonium phosphate and determined as $Mg_2P_2O_7$.

In the case of calcium and magnesium, reprecipitation is essential in order to get satisfactory results.

(i) 34–44 mg of strontium could be separated from 29 [illegible] mg of rhenium and 15–20 mg of platinum.
(ii) 40–50 mg of calcium could be separated from 29–3[illegible] of rhenium and 17–23 mg of platinum.
(iii) 12–16 mg of magnesium could be separated from 29–37 mg of rhenium and 17–23 mg of platinum.

The metals were recovered with an accuracy of

Sr: −0.21 to + 0.1% and Re: −0.17 to + 0.07%;
Sr: −0.21 to + 0.14% and Pt: −0.33 to + 0.06%;
Ca: 0.0 to −0.3% and Re: + 0.07 to −0.16%;
Ca: 0.0 to −0.24% and Pt: + 0.36 to −0.27%;
Mg: + 0.12 to −0.3% and Re: ± 0.16%;
Mg: + 0.0 to −0.3% and Pt: + 0.27 to −0.39%.

Separation of gold or mercury from strontium, calcium or magnesium

Standard solutions of auric chloride, mercuric chloride[12], strontium chloride, calcium chloride and magnesium chloride were used. Measured volumes of the solutions of two ions were mixed and the procedure given for the separation of gold from barium was followed. Gold was determined as Au_2S_3 and mercury as HgS.

In the filtrate, strontium was determined as $SrSO_4$, calcium as calcium oxalate monohydrate or calcium carbonate, and magnesium as $Mg_2P_2O_7$.

34–44 mg of strontium, 40–50 mg of calcium and 12–16 mg of magnesium could be separated from 17–33 mg of gold or 73–92 mg of mercury.

The metals were recovered with an accuracy of

Sr: −0.21 to + 0.1% and Au: 0.0 to −0.25%;
Sr: 0.0 to −0.26% and Hg: + 0.05 to −0.18%;
Ca: 0.0 to −0.24% and Au: ± 0.25%;
Ca: 0.0 to −0.3% and Hg: + 0.06 to −0.1%;
Mg: + 0.08 to −0.3% and Au: + 0.17 to −0.37%;
Mg: + 0.12 to −0.3% and Hg: 0.0 to −0.19%.

Separation of bismuth, palladium, lead or cadmium from strontium, calcium or magnesium

Measured volumes of standard solutions of two ions were mixed and the procedure given for the separation of these metals from barium was followed. Bismuth, palladium, lead and cadmium were determined as sulphides. In the filtrate, strontium was determined as $SrSO_4$, calcium as calcium oxalate monohydrate or calcium carbonate, and magnesium as $Mg_2P_2O_7$.

(i) 34–44 mg of strontium could be separated from 37–47 mg of bismuth, 25–32 mg of palladium, 57–73 mg of lead or 46–59 mg of cadmium.

(ii) 40–50 mg of calcium could be separated from 49–62 mg of bismuth, 23–30 mg of palladium, 57–73 mg of lead or 40–50 mg of cadmium.

(iii) 12–16 mg of magnesium could be separated from 49–62 mg of bismuth, 23–30 mg of palladium, 54–68 mg of lead or 35–45 mg of cadmium.

The metals were recovered with an accuracy of

Sr: + 0.15 to −0.26% and Bi: + 0.15 to −0.24%;
Sr: + 0.1 to −0.26% and Pd: 0.0 to −0.25%;
Sr: 0.0 to −0.26% and Pb: 0.0 to −0.27%;
Sr: 0.0 to −0.26% and Cd: 0.0 to −0.26%;
Ca: 0.0 to 0.3%, Bi: + 0.13 to −0.25% and Pd: + 0.2 to −0.24%,
Pb: + 0.11 to −0.07% and Cd: + 0.14 to 0.2%;
Mg: 0.0 to −0.3% and Bi: + 0.13 to −0.16%;
Mg: + 0.23 to −0.3% and Pd: 0.0 to −0.23%;
Mg: + 0.12 to −0.32% and Pb: ± 0.16%;
Mg: + 0.12 to −0.32% and Cd: + 0.16 to −0.22%.

SUMMARY

It has been shown that 2*N* sodium sulphide reagent can be used efficiently for separating:

1. Barium from rhenium, platinum, gold, bismuth, palladium, lead or cadmium.
2. Strontium, calcium and magnesium from rhenium, platinum, gold, mercury, bismuth, palladium, lead or cadmium.

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Received December 17th, 1957

SEPARATIONS INVOLVING SULPHIDES

VII. SEPARATION OF (A) BISMUTH, LEAD AND CADMIUM FROM MERCURY, AND (B) BISMUTH AND MERCURY FROM INDIUM

by

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The quantitative separation of mercury from a number of elements forming thiosalts has already been dealt with in previous papers[1]. In this paper, methods of estimating mercury in the presence of certain metals of the copper group and indium are given.

EXPERIMENTAL

(*a*) (*i*) *Separation of mercury from bismuth*

Measured volumes of standard solutions of bismuth chloride[2] and mercuric chloride[3] were mixed and treated with ammonium hydroxide till a slight turbidity appeared. In one set of experiments the mixture was treated with 50–70 ml of 2*N* sodium sulphide reagent[4] followed by 10–15 g of ammonium acetate (solid) and shaken for a minute to precipitate the metals completely as sulphides. The precipitate of the mixed sulphides was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with water, alcohol and ether successively, dried in an air oven at 105° for 1 h and weighed. In the second series of experiments, after adding sodium sulphide reagent, the mixture was treated with enough 12*N* hydrochloric acid to give a final acidity of a little above 6*N*. The mixture was heated to boiling to dissolve bismuth sulphide and completely precipitate mercury as mercuric sulphide. The precipitate of mercuric sulphide was filtered through a weighed sintered glass crucible (porosity 4), washed 4–5 times with 5–10 ml portions of hot 6*N* hydrochloric acid, then thoroughly with water, alcohol and ether successively, dried in an air oven at 105° for 1 h and weighed as HgS. The weight of the precipitated bismuth trisulphide was determined by difference.

80–100 mg of mercury could be separated from 83–105 mg of bismuth. The metals were recovered with an accuracy of

Hg: 0.0 to -0.19% and Bi: 0.0 to -0.2%.

(*a*) (*ii*) *Separation of mercury from lead*

Measured volumes of standard solutions of lead acetate[2] and mercuric chloride were mixed and treated with ammonia (sp.gr. 0.88) to neutralize the acid. In one set of experiments the mixture was treated with 45–70 ml of 2*N* sodium sulphide reagent followed by enough 6*N* acetic acid to give a final acidity of about 3*N*. The mixture was heated to boiling to precipitate both the metals as sulphides. The precipitate of the mixed sulphides was filtered through a weighed sintered glass crucible (porosity 4) and after suitable treatment[2] dried in vacuum for $^1/_2$ h and weighed. In the second series of experiments the procedure given above for the precipitation of mercury as sulphide with 2*N* sodium sulphide and 12*N* hydrochloric acid was followed and mercury estimated as HgS. The weight of the precipitated lead sulphide was determined by difference.

74–187 mg of mercury could be separated from 60–150 mg of lead. The metals were recovered with an accuracy of

Hg: $+0.02$ to -0.1% and Pb: $+0.07$ to -0.09%.

(a) (iii) Separation of mercury from cadmium

Standard solutions of cadmium sulphate[2] and mercuric chloride were mixed. The procedure given for the separation of lead from mercury was followed. The precipitate of the mixed sulphides was washed with hot 3*N* acetic acid (to prevent peptization) and then thoroughly with alcohol and ether successively, dried at 105° for 1 h and weighed. Mercury was estimated as HgS and cadmium as CdS.

74–187 mg of mercury could be separated from 52–131 mg of cadmium. The metals were recovered with an accuracy of

$$\text{Hg}: +0.12 \text{ to } -0.07\% \text{ and Cd}: +0.08 \text{ to } -0.25\%.$$

In the separations given above bismuth cannot be estimated in the filtrate from mercuric sulphide since results obtained are too high, but lead[5] and cadmium[6] can be so estimated.

(b) Separation of indium from mercury or bismuth

Measured volumes of standard solutions of indium chloride[2] and mercuric chloride or bismuth chloride were mixed and the free acid, if any, neutralized by adding ammonium hydroxide in slight excess. The mixture was treated with 25–35 ml of 2*N* sodium sulphide reagent followed by enough 3*N* hydrochloric acid to give a final acidity of about 1*N*. The precipitate of mercuric or bismuth sulphide was washed with 1*N* hydrochloric acid (the filtrate reserved for the estimation of indium) and after suitable treatment[3] weighed as HgS or Bi_2S_3.

The filtrate was concentrated to about 25 ml, the free acid neutralized with ammonia (sp.gr. 0.88), the hot solution was cooled in ice and treated with 15–25 ml of 2*N* sodium sulphide reagent followed by enough 6*N* acetic acid to give a final acidity of about 3*N*. The precipitate of indium sulphide was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with alcohol and ether successively, dried at 105° for 1 h and weighed as In_2S_3.

20–25 mg of indium could be separated from 80–102 mg of mercury and 23–30 mg of indium from 39–49 mg of bismuth. The metals were recovered with an accuracy of

$$\text{In}: 0.0 \text{ to } -0.35\% \text{ and Hg}: 0.0 \text{ to } -0.11\%;$$
$$\text{In}: \pm 0.24\% \text{ and Bi}: 0.0 \text{ to } -0.33\%.$$

Note

It is not possible to estimate mercury in the presence of copper, nickel, cobalt, thallium, rhodium and palladium by this method, because the sulphides of these metals do not dissolve completely in 6*N* hydrochloric acid unles an oxidizing agent is present.

SUMMARY

It has been shown that 2*N* sodium sulphide reagent can be successfully used in the separation and estimation of:
(a) bismuth, lead and cadmium from mercury, and
(b) bismuth and mercury from indium.

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Received January 6th, 1958

THE *T*-EFFECT: A METHOD FOR INCREASING RESOLUTION IN SOME SYSTEMS IN WHICH SUBSTANCES TRAVERSE A MEDIUM AT DIFFERENT RATES

by

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Resolution of substances separable by processes in which the substances traverse a medium at different rates can sometimes be improved without increasing the total time of traverse, if two media are used in tandem and one or more of the substances enter the second medium. The improvement in resolution is independent of the nature of the forces responsible for the rate differentials. This change in resolving power is termed the tandem-transfer or *T*-effect.

The discussion below, therefore, applies to column and paper chromatography, ion-exchange columns and papers, electrophoresis, particle classification, distillation in packed columns, production of spectra by diffraction of light, etc. It does not apply to separations in which successive changes in conditions are applied simultaneously to all the substances being separated, such as two-dimensional chromatography, counter-current distribution, and separations treated by plate theory.

Given

1. Media X and Y placed in tandem
2. Substances A and B traversing first medium X and then medium Y
3. Substance A has rate of traverse of medium X of A_x/unit time
   Substance B has rate of traverse of medium X of B_x/unit time
   Substance A has rate of traverse of medium Y of A_y/unit time
   Substance B has rate of traverse of medium Y of B_y/unit time
4. The time substance A is moving in medium X is T_{ax}
   The time substance B is moving in medium X is T_{bx}
   The time substance A is moving in medium Y is T_{ay}
   The time substance B is moving in medium Y is T_{by}
5. Media X and Y are defined by the condition that the difference between the rates of traverse of A and B is greater in X than in Y $[(B_x - A_x) > (B_y - A_y)]$
6. Substances A and B are defined by the condition that $B_x > A_x$
7. The substances migrate in infinitely thin bands without spreading during migration. (Note: If bands spread, the general treatment holds if the rates for the trailing edge of the faster component and the leading edge of the slower component are considered.)

Required

The relationships necessary to give an increase in resolution by the tandem-transfer process over that obtainable using either medium X or medium Y, if the total time is held constant.

Solution

The distance, D_A, moved by substance A in time S is equal to $A_x \cdot T_{ax} + A_y \cdot T_{ay}$
The distance, D_B, moved by substance B in time S is equal to $B_x \cdot T_{bx} + B_y \cdot T_{by}$
The distance, D, between A and B at any given time is given by

$$D = (B_x \cdot T_{bx} + B_y \cdot T_{by}) - (A_x \cdot T_{ax} + A_y \cdot T_{ay}) \quad \ldots\ldots\ldots (1)$$

Since, by definition, $(B_x - A_x) > (B_y - A_y)$ and $B_x > A_x$, it is apparent from (1) that D is a maximum for $T_{ay} = 0$. Therefore medium X must make up the first portion of the tandem arrangement.

If the total time during which separation is taking place is S, then for $T_{ay} = 0$, $T_{ax} = S$.

$$D = (B_x \cdot T_{bx} + B_y \cdot T_{by}) - A_x \cdot S \quad \ldots\ldots\ldots (2)$$

Consider using only medium X; $T_{bx} = S$, $B_x > A_x$, then $D' = (B_x - A_x)S$.

The difference between the separation on medium X and by the tandem-transfer technique is now:

$$D - D' = (B_x \cdot T_{bx} + B_y \cdot T_{by}) - B_x \cdot S \quad \ldots\ldots\ldots (3)$$

For the separation by the tandem-transfer technique to be greater than in medium X alone, it is necessary that $D > D'$ or

$$(B_x \cdot T_{bx} + B_y \cdot T_{by}) - B_x \cdot S > 0 \quad \ldots\ldots\ldots (4)$$

Substituting $T_{bx} = (S - T_{by})$, the condition of (4) is met only if $B_y > B_x$.

In summary, then, maximum resolution for a given time, S, will be accomplished by the tandem-transfer technique if $B_y > B_x$ and if $T_{ay} = 0$, that is, if the length of medium X is so chosen that A just reaches the end in time S, and if Y is long enough so that B is retained in Y.

For multicomponent systems, separations may be calculated from (1) by taking the components in pairs, or may be more easily visualized by a graphical solution in which the distance travelled by each component is plotted against time. The slopes of the various curves will correspond to the rates. The vertical distances between any two curves is then the distance between the two components at a given time. If an arbitrary length for medium X is chosen, the total time required to obtain the desired separation may be read from the graph. If this time required is considered as a multiple of the time desired, the arbitrary length of X chosen may now be considered a multiple of the desired length, and the length of medium X needed to obtain the desired separation in the desired time can be calculated by simple proportion.

This effect may be applied in reverse to reduce the width of bands which have broadened more than desired during the separation process. Thus, if the leading edge of the band is considered as substance B and the trailing edge as substance A, since B_x is greater than A_x, and B_y is greater than A_y, by definition of a broadening band, if $B_y - A_x$ is less than both $B_x - A_x$ and $B_y - A_y$, the band will narrow during the tandem-transfer process. This change in band width in continuous zone electrophoresis in a gradient containing discrete concentration zones has been mentioned by INGER BRATTSTEN[1].

SUMMARY

By placing two media in tandem (T-effect), resolution can sometimes be increased without increasing the time required for separation in chromatography, ion-exchange, electrophoresis, distillation, particle classification, production of spectra by refraction of light, etc. Conditions necessary for this increase in resolution are derived mathematically. Optimum conditions for maximum resolution are calculated.

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Received December 17th, 1957

USE OF THE TANDEM-TRANSFER TECHNIQUE IN THE RAPID SEPARATION ON ION-EXCHANGE RESIN PAPERS OF PHENYLALANINE AND TYROSINE FROM MIXTURES OF AMINO ACIDS

by

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INTRODUCTION

A previous paper[1] reported the rapid separation of arginine, histidine, and lysine on a sulfonic acid type cation-exchange resin paper. Under the specified conditions, however, the aromatic amino acids present in the casein hydrolyzates, phenylalanine and tyrosine, could not be separated from each other. Since variation of the hydrogen ion concentration of the developing buffer is not very effective in changing the relative positions of the amino acids over the short solvent path used, it was decided to attempt the separation of these two aromatic amino acids on a carboxylic acid-type cation-exchange resin paper. Carboxylic acid ion-exchange resins have been used by several investigators[2-9] for the separation of dibasic amino acids from mixtures.

EXPERIMENTAL

In December 1956 an experimental carboxylic acid ion-exchange resin paper was made available to some investigators by the Rohm and Haas Co., Philadelphia, Pa. It contains about 28%, by weight, of Amberlite IRC-50 (H^+) type cation-exchange resin. From data supplied by the company, this paper has an exchange capacity of about 8 μequiv./cm^2.

Six μl of 0.02M solutions of various amino acids were spotted across a sheet of the ion-exchange paper and developed at 25° by descending chromatography with various buffer mixtures, allowing the solvent front to progress 22 cm beyond the point of sample application. The sheets were air-dried, sprayed with ninhydrin (1,2,3-triketohydrindene) reagent (1.00 g ninhydrin in 400 g absolute alcohol denatured with 0.5% benzene, 150 g dichlorodifluoromethane, and 600 g dichlorotetrafluoroethane, packed in aerosol spray cans), and examined after 1 h. A schematic diagram of the sheet on which a pH 5.2 acetate buffer 0.2*M* in sodium acetate was used for development is shown in Fig. 1. This buffer was chosen from a group covering the range from pH 1.2 to pH 6.8 because it gave the maximum separation between phenylalanine and tyrosine.

Approximately 6 μl of various standard solutions 0.02*M* in amino acid were streaked across strips of ion-exchange paper 3 cm wide by 30.5 cm long, developed, sprayed with ninhydrin reagent, and read in a recording densitometer as previously described[1]. Average R_F values based on half the band width at half the band height and their standard deviation calculated by the method of DEAN AND DIXON[10] are listed in Table I.

Superimposition of the photometer traces of lysine, phenylalanine, tyrosine and leucine showed that a mixture of these four amino acids would give two broad bands, one containing lysine and phenylalanine; the other, tyrosine and leucine. From Fig. 1 it was expected that a mixture of the amino acids would show the following bands: (a) arginine and histidine, (b) lysine and phenylalanine, (c) tyrosine, leucine, isoleucine and methionine, (d) valine, glycine, alanine, serine, threonine. A mixture of these amino acids did give four bands when threated as described above.

TABLE I

INDIVIDUAL AMINO ACIDS ON IRC-50 (H$^+$) TYPE-ION-EXCHANGE PAPER developed with pH 5.2 acetate buffer at 25°. Length of developer path is 22 cm

	cm from point of application			
	Lysine	*Phenylalanine*	*Tyrosine*	*Leucine*
	12.2	13.8	16.4	17.6
	11.6	13.5	16.4	17.3
	11.7	13.3	16.1	17.4
	11.7	13.2	16.2	17.4
Average	11.8	13.5	16.3	17.4
100 R_F	53.6	61.3	74.0	79.0
Standard Deviation	1.3	1.3	0.4	0.4

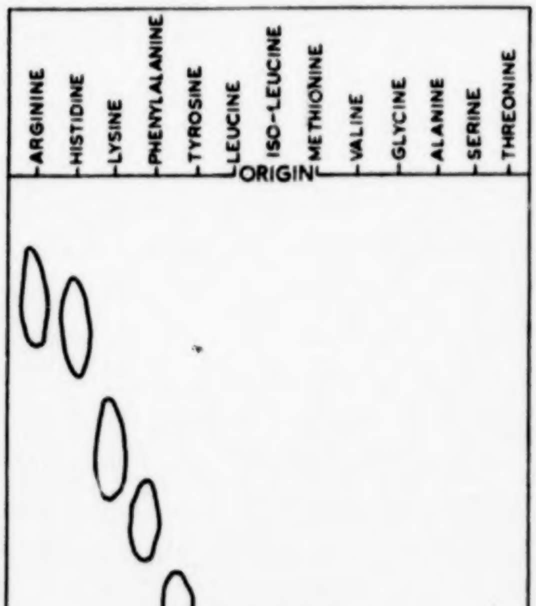

Fig. 1. Location of zones of individual amino acids on IRC-50 (H$^+$) type ion-exchange paper developed with pH 5.2 acetate buffer at 25°.

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If the time required for the separation of the amino acids is not an important factor, bands a, b, and c above may be individually cut from the strip, eluted, and rerun on Amberlite IR-120 (Na^+) type paper as previously described[1] to obtain arginine, histidine, lysine, phenylalanine and tyrosine in bands free of the other amino acids. The rest of the amino acids are not resolved by this technique.

Since it was desired to keep the time required for the separation to a minimum, rerunning the mixed bands was unsatisfactory. Calculations using the tandem-transfer technique[11] were made as described below:

The R_F values obtained for the amino acids on the IR-120 (Na^+) type paper previously reported[1] and the R_F values obtained for the amino acids on IRC-50 (H^+) type paper listed in Table I were converted into rate of movement of the band, assuming that the rate of developer flow on both papers is about 20 cm/h. These values are listed in Table II.

TABLE II

CALCULATED RATE OF MOVEMENT OF AMINO ACIDS ON ION-EXCHANGE PAPERS using a pH 5.2 acetate buffer at 25°

	cm/h	
	IR-120 (Na^+) type	*IRC-50 (H^+) type*
Lysine	4.7	10.7
Phenylalanine	12.2	12.3
Tyrosine	12.2	14.8
Leucine	17.8	15.8

Assuming a tandem strip in which the path length is 2 cm of IR-120 (Na^+)-type paper plus 20 cm of IRC-50 (H^+)-type paper, from the values in Table II a graph showing the distance moved by each amino acid at any given time can be drawn (Fig. 2).

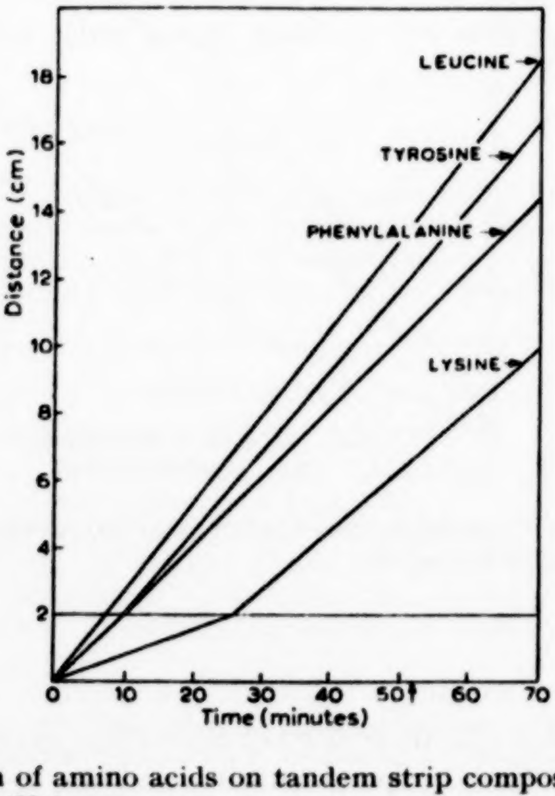

Fig. 2. Calculated separation of amino acids on tandem strip composed of 2 cm of IR-120 (Na^+) paper plus 20 cm of IRC-50 (H^+) paper.

Examination of this graph shows that lysine will be well separated, but phenylalanine, tyrosine, and leucine will lie closer together. Further examination shows that the separation between phenylalanine and tyrosine equals the separation between tyrosine and leucine at about 52 min. At

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this time the separation is 1.6 cm. Since the total time is to be held constant at 66 min (total path length of 22 cm) the ratio of the time desired to the time found is 66/52 or approximately 1.25.

Using this last factor as a multiplier, it can now be predicted that for a 22-cm path composed of 2.5 cm (1.25 × 2 cm) of IR-120 (Na^+) paper and 19.5 cm of IRC-50 (H^+) paper, and using a 66-min development time, the separation between the above named pairs of amino acids will be 2 cm (1.25 × 1.6 cm). The values in Table II, re-graphed for these new calculated conditions are shown in Fig. 3.

The tandem strips were prepared by joining 8.5 cm of IR-120 (Na^+) paper to 30.5 cm of IRC-50 (H^+) by use of cellophane tape, overlapping the papers about 2 mm. A pencil line was drawn 6 cm from the beginning of the IR-120 (Na^+) portion of the strip, and another pencil line 22 cm below the first. The seemingly large excess length of the strip is explained below.

About 6 μl of a solution containing lysine, phenylalanine, tyrosine, and leucine, 0.02 *M* in each amino acid, were streaked across the papers at the 6-cm mark and developed by conventional descending chromatography in a chamber saturated with water vapor at 25°, using the pH-5.2 acetate buffer; until the developer front reached the 22-cm mark. The strips were removed from the chamber, air-dried, sprayed with ninhydrin reagent, and allowed to develop color at 25° for 1 h, then at 100° for 10 min. A permanent record was obtained by reading the strips in a recording densitometer. The values obtained and their standard deviations, and the values calculated from Fig. 3 are shown in Table III. Extra length was left on the strips because some difficulty was experienced with the densitometer due to the sudden increase in thickness at the point at which the strips overlap. To obviate this difficulty, the tandem strips were fed into the densitometer with the IRC-50 (H^+) portion first.

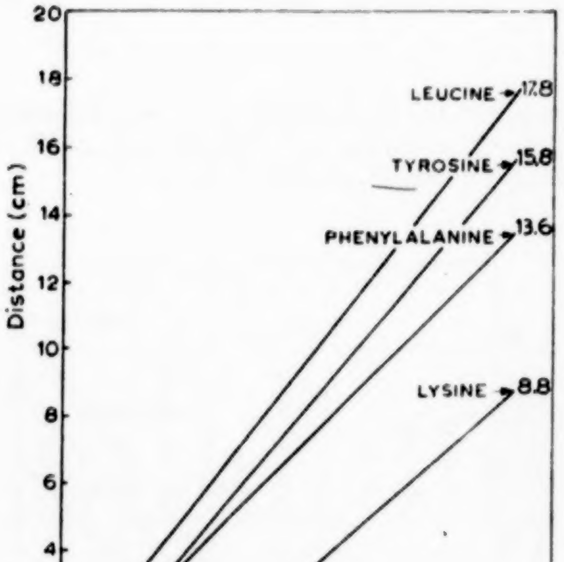

Fig. 3. Calculated separation of amino acids on tandem strip composed of 2.5 cm of IR-120 (Na^+) paper plus 19.5 cm of IRC-50 (H^+) paper.

DISCUSSION

As can be seen from Table III, there is good agreement between the average distance moved by the amino acid found experimentally, and the values calculated. From the magnitudes of the standard deviations, it is apparent that the position of the amino acid on the developed strip is characteristic for the substance and can be used as a means of identification.

As might be expected from the relationships between the rates of movement of the

TABLE III

VALUES FOR DISTANCE OF MIGRATION OF AMINO ACIDS ON A TANDEM STRIP

using 2.5-cm path in IR-120 (Na$^+$) type paper followed by IRC-50 (H$^+$) type paper. Developed with pH 5.2 acetate buffer. Length of developer path is 22 cm

	Distance moved in cm			
	Lysine	*Phenylalanine*	*Tyrosine*	*Leucine*
Found	8.1	13.8	15.9	17.7
	7.5	13.6	15.8	17.8
	8.4	14.2	16.1	17.8
	7.7	14.1	15.9	17.9
	7.8	14.0	16.6	18.0
	8.5	14.4	16.2	18.2
Average	8.0	14.0	16.0	17.9
Standard Deviation	0.4	0.2	0.3	0.2
Calculated	8.8	13.6	15.8	17.8

amino acids on the IR-120 (Na$^+$) type paper and the IRC-50 (H$^+$) type paper listed in Table II, and from the discussion of the tandem-transfer effect[11], the band obtained for lysine (as well as those obtained for arginine and histidine) on the tandem strips described, was very much broadened, whereas the band for leucine was somewhat narrower than that obtained on the IR-120 (Na$^+$) paper.

In summary, therefore, the method described gives a sharp separation of phenylalanine and tyrosine, from each other, and from the other amino acids found normally in casein hydrolyzates, but other amino acids in the mixture are not well differentiated.

SUMMARY

Using the tandem-transfer technique (*T*-effect), the aromatic amino acids, phenylalanine and tyrosine, have been isolated from casein hydrolyzates and simultaneously separated from each other by one-step chromatography on cation-exchange papers. The total development time is about 80 min, using a 0.2*M*, pH-5.2 acetate buffer. Calculations of the optimum conditions for the separation are shown.

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Received December 17th, 1957

THE USE OF NAPHTHALENE DERIVATIVES IN INORGANIC ANALYSIS

VI. A NEW REAGENT FOR THE FLUORIMETRIC DETECTION OF TIN

by

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INTRODUCTION

The application of the nitro-aminonaphthalene monosulphonic acids[1-3] to the detection and estimation of stannous tin has already been reported in earlier papers of this series. The use of the nitronaphthylamines[4] for the detection of stannous tin has also been described. In this communication a more sensitive reagent, 6-nitro-2-hydroxynaphthalene-8-sulphonic acid is reported for the fluorimetric detection of stannous tin. Using a method previously described[1,3], 55 metallic ions were examined and only stannous tin gave an intense fluorescence when viewed under ultraviolet light, after quenching of any initial fluorescence with $15N$ NH_4OH.

EXPERIMENTAL

Synthesis of reagent

The mononitration of 2-aminonaphthalene-8-sulphonic acid according to the method of FRIEDLANDER AND LUCHT[5] yielded 6-nitro-2-aminonaphthalene-8-sulphonic acid. The ammonium salt (10.0 g) of this acid was diazotised as a paste in water (80 ml) using the "inverted method". Crushed ice (60 g) was added followed by concentrated HCl (14 ml) and the slurry diazotised at 0–5° by the addition of sodium nitrite (3.0 g) in water (20 ml) over a period of 5 min. The mixture was stirred at 0–5° for 2 h after which the precipitated pale yellow diazonium salt was filtered, then added to $2N$ H_2SO_4 (400 ml) and the solution gradually brought to the boil on the hot plate. Boiling was continued until complete evolution of nitrogen ceased and the sulphuric acid solution gave no colour reaction with alkaline phenol. The solution was filtered hot, concentrated on a steam bath, then cooled, the yellow needles of 6-nitro-2-hydroxynaphthalene-8-sulphonic acid being filtered and recrystallised from 50% aqueous alcohol.

The ammonium salt of this acid was prepared by dissolving the free acid in hot 50% aqueous alcohol and neutralizing the solution with ammonium carbonate. The yellow ammonium salt was recrystallised from hot water.

Analysis – Ammonium salt

Calculated for $C_{10}H_{10}O_6N_2S$:	C 41.95; H 3.52; N 9.79.
Found:	C 41.41; H 3.45; N 10.06.

The barium salt was obtained by neutralizing a hot 50% aqueous alcohol solution of the free acid with $BaCO_3$. The solution was filtered hot then cooled, and the orange barium salt which precipitated was re-crystallised from hot water.

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* On study leave at Birkbeck College, University of London (Great Britain).

Analysis – Barium salt

Calculated for $C_{20}H_{12}O_{12}N_2S_2Ba.3H_2O$: C 33.00; H 2.49; Ba 18.88.
Found: C 33.16; H 2.59; Ba 18.95.

Barium was estimated as $BaSO_4$ by digestion of the compound with concentrated sulphuric acid.

6-Nitro-2-hydroxynaphthalene

A solution of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid (1.0 g) in 10*N* HCl (10 ml) was carefully heated to 160° for 2 h in a sealed glass tube, then cooled. The solution was diluted with H_2O (90 ml), the precipitate (0.48 g) filtered dried and recrystallised from benzene to give pale yellow needles. (M.P. 158–9°) This compound showed no depression of melting point when mixed with an authentic sample of 6-nitro-2-hydroxy-naphthalene prepared from 6-nitro-2-amino-naphthalene by a diazotisation procedure*, thus confirming the orientation of the nitro group in the original compound.

Technique of spot testing

The standard procedure reported in previous communications[1,3,4] was used. All fluorescence tests were carried out using a Crompton electric discharge lamp, (125 W, 230/240 V) with a wave length of approximately 3650 Å U.V. radiation. A 0.1% aqueous solution of the ammonium salt of 6-nitro-2-hydroxynaphthalene-8-sulphonic acid was used as reagent in these tests, the results of which are shown in Table I.

TABLE I

COLOUR AND FLUORESCENCE UNDER ULTRA-VIOLET LIGHT OF SPOTS OF IONS AFTER SPRAYING WITH REAGENT BEFORE AND AFTER TREATMENT WITH 15*N* NH_4OH

Ion	*Before spraying with 15N NH_4OH*	*After spraying with 15N NH_4OH*
[a] Ce^{+4}	Purple	Violet
Fe^{+2}	Brown-violet	Pale brown
Sb^{+3}	Pale purple	Yellow (faint fluorescence)
As^{+3}	Purple	Yellow (faint fluorescence)
As^{+5}	Yellow (faint fluorescence)	Pale violet
W^{+6}	Orange-red	Pale orange-red
Sn^{+2}	Dark purple (faint fluorescence)	Intense blue fluorescence
Fe^{+3}	Brown-violet	Violet-brown
Au^{+3}	Dark violet	Brown
Hg^{+}	Pale violet	Pale brown
Hg^{+2}	Pale violet	Pale brown
Cr^{+6}	Dark violet-brown	Dark violet-brown
Be^{+2}	Yellow (faint fluorescence)	Yellow (faint fluorescence)
Th^{+4}	Faint purple	Pale orange
Bi^{+3}	Pale violet	Yellow (faint fluorescence)
VO_4^{-3}	Red	Red

[a] A freshly prepared aqueous solution of ceric ammonium nitrate (AR grade) was used.

Other ions tested included:

Li^{+}, Na^{+}, K^{+}, Cu^{+2}, Ag^{+}, Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Zn^{+2}, Cd^{+2}, La^{+3}, Pb^{+2}, Mo^{+6}, Te^{+6}, Mn^{+2}, Co^{+2}, Ni^{+2}, Pt^{+2}, Ce^{+3}, VO^{+2}, Cr^{+3}, UO_2^{+2}, Ti^{+4}, Al^{+3}, Ga^{+3}, In^{+3}, Tl^{+}, Tl^{+3}, Sn^{+4}, Zr^{+4}, Pd^{+2}, Pt^{+4}, VO_3^{-}, Rb^{+}, Cs^{+}, Ti^{+3}, Ru^{+3}, ZrO^{+2}.

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* Authentic sample of 6-nitro-2-hydroxy-naphthalene was kindly supplied by Dr. A. BRYSON, N.S.W. University of Technology, Sydney, Australia.

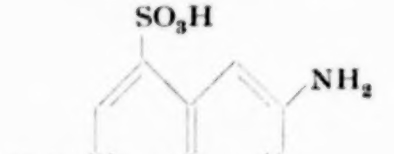
The data in Table I indicate that only Sn^{+2} exhibits intense blue fluorescence under the conditions of test, the remaining ions tabulated yielding coloured spots which were non-fluorescent.

Sensitivity tests

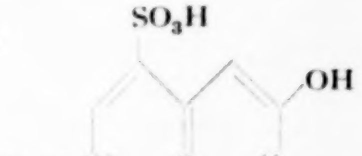
Sensitivity tests for stannous tin were performed using a conventional procedure[1,3,4], a 0.1% aqueous solution of the ammonium salt of 6-nitro-2-aminonaphthalene-8-sulphonic acid being used as a standard reagent[1] for comparative purposes. Using a 0.1% aqueous solution of the ammonium salt of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid, spots containing 10^{-6} g stannous tin exhibited a blue fluorescence whilst lower concentrations (10^{-7} to 10^{-12} g) gave faintly fluorescent spots, sulphur-yellow in colour. Blank tests performed with a *N* HCl solution and the new reagent, yielded yellow spots with very faint fluorescence. The fluorescence intensity of these blanks was similar to that exhibited by concentrations of stannous tin from 10^{-9} to 10^{-12} g.

DISCUSSION

It has been shown that when 6-nitro-2-aminonaphthalene-8-sulphonic acid is used as a fluorimetric reagent for stannous tin[1,2], the fluorescence can be attributed to the formation of 2,6-diaminonaphthalene-8-sulphonic acid (A).



(A)



(B)

When 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid is used as a reagent in the same test, it is suggested that reduction of the nitro group occurs to yield the corresponding amino-derivative (B) which is the compound responsible for the fluorescence.

Since the substitution of an OH group for an NH$_2$ group in the original 6-nitro-2-amino-naphthalene-8-sulphonic acid reagent produces a derivative which yields a slightly more sensitive fluorescent test with stannous tin than does the parent compound, it can be said that the contribution of the hydroxyl group to the excited state of (B) is greater than the contribution of the corresponding amino group to the excited state of (A). This result is in keeping with the published observation that the presence of hydroxyl groups in a molecule will enhance the fluorescent properties of that particular compound[6]. Present tests have been limited to those of a qualitative nature but in future experiments, it is hoped to obtain some quantitative information concerning the relative effect of these different substituents in the naphthalene nucleus upon the sensitivity of test.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the gift of 2-aminonaphthalene-8-sulphonic acid from Geigy (Austral.) Ltd. by Mr. J. T. SNELSON.

The authors are also indebted to Dr. E. CHALLEN of the N.S.W. University of Technology, Micro-analytical Laboratory for all C, H and N analyses reported in this paper.

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One of us, J. R. A. Anderson, wishes to thank Professor W. WARDLAW for permission to carry out part of this work at the Department of Chemistry, Birkbeck College, University of London (Great Britain).

SUMMARY

The use of 6-nitro-2-hydroxy-naphthalene-8-sulphonic acid as a new fluorimetric reagent for the detection of tin has been reported. This reagent is capable of detecting 10^{-8} g stannous tin under the conditions of the test and is slightly more sensitive for this purpose than the previously recommended 6-nitro-2-aminonaphthalene-8-sulphonic acid.

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Received December 10th, 1957

DÉVELOPPEMENT PAR DÉPLACEMENT SUR ÉCHANGEURS D'IONS
SÉPARATION DE PLUS DE DEUX IONS

par

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Dans un précédent mémoire[1], nous avons montré que la connaissance de la constante de l'équilibre de deux ions entre une solution et une résine permet de calculer la distance à faire parcourir à une bande contenant les deux corps pour que ceux-ci soient répartis en deux zones jointives. Il est possible de généraliser les résultats obtenus à la séparation d'un nombre quelconque d'ions. Nous envisagerons d'abord le cas de trois corps.

CAS DE TROIS IONS

Fixation des ions sur la résine

On introduit, d'une manière continue, une solution contenant les ions M_1, M_2, M_3 aux concentrations respectives C_1, C_2, C_3 dans une colonne contenant une résine sous forme M_0 de capacité C_R. Nous supposerons que l'affinité des différents ions pour la résine est dans l'ordre: $M_0 < M_1 < M_2 < M_3$. Comment se répartissent les différents ions dans la colonne, lorsqu'une longueur l de résine a été mise en jeu? La partie supérieure de la résine se met en équilibre avec la solution influente et comme M_3 se fixe mieux que M_1 et M_2, il y aura un excès de ces deux ions en tête. Enfin, comme M_2 a plus d'affinité que M_1, il y aura également un excès de M_1 en tête de la zone contenant M_1 et M_2. Les ions sont donc répartis dans la résine en 3 bandes de longueur respective l_1, l_2 et l_3 (Fig. 1) que l'on se propose de déterminer. On ne peut plus, comme dans le cas de deux ions, calculer ces longueurs à l'aide des volumes de rétention. En effet ces derniers indiquent l'apparition des solutés dans l'effluent à des instants différents et le problème qui nous intéresse ici est celui de la position relative des divers isochromes. Les deux problèmes pourraient être traités simultanément dans le cas de la séparation de deux corps, car il n'apparaissait qu'une bande en tête ou en queue de la bande initiale. Ici, il s'en forme deux (Fig. 1). Dans le cas de *n* corps il y en aurait *n*—1. Pour calculer les longueurs des 3 bandes, il suffit d'écrire que la quantité de chaque soluté introduite est égale à la somme des quantités fixées sur la résine dans chacune des zones. Pour cela, il faut connaître les concentrations dans la résine. Dans la première bande M_1 est pur, il est donc à la concentration C_R. Dans la deuxième bande, la somme des concentrations de M_1 ($C'1R$) et de M_2 ($C'2R$) est égale à C_R et leur rapport est le même que dans la dernière zone à condition que M_3 ne modifie pas l'équilibre existant entre les deux ions. Enfin dans la troisième zone, la somme des trois concentrations est égale à C_R et on dispose des deux lois d'action de masses des équilibres entre M_1 et M_2 d'une part et M_1 et M_3 d'autre part, par exemple. On en déduit, comme dans le cas de deux ions, que la concentration de M_1 est de la forme:

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$$C_{1R} = \frac{K_1C_1 \cdot C_R}{K_1C_1 + K_2C_2 + K_3C_3}$$

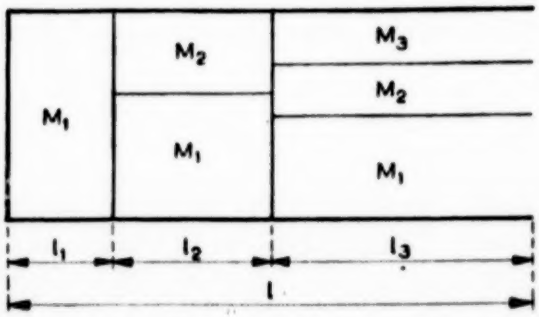

Fig. 1. Répartition des solutés dans la résine au cours d'une fixation.

Les formules donnant les concentrations de M_2 et M_3 s'obtiendraient en permutant respectivement les indices 1 et 2 ou 1 et 3 dans la relation précédente.

Lorsqu'il est passé un volume V d'influent, de concentration totale C_0, à travers la colonne, une masse m de longueur l de résine est saturée de M_1, M_2 et M_3 répartis comme il a été vu précédemment.

On a:

$$m\,C_R = V\,C_0$$

De plus si m_3 est la masse de résine contenue dans la deuxième bande, le bilan de M_3 est:

$$m_3\,C_{3R} = V\,C_3$$

or

$$\frac{m_3}{m} = \frac{l_3}{l}$$

Des trois relations précédentes, on déduit:

$$l_3 C_R = l C_R \frac{C_3}{C_0}$$

De la même manière les bilans de M_2 et M_1 peuvent être mis sous la forme:

$$l_2 C'_{2R} + l_3 C_{2R} = l C_R \frac{C_2}{C_0}$$

et

$$l_1 C_R + l_2 C'_{1R} + l_3 C_{1R} = l C_R \frac{C_1}{C_0}$$

On dispose d'un système de trois équations à trois inconnues l_1, l_2 et l_3, les concentrations dans la résine étant calculées comme il a été dit précédemment. Il vient:

$$l_1 = l \cdot \frac{C_1}{C_0} \cdot \frac{K_2 - K_1}{K_2} \quad \ldots\ldots (1)$$

$$l_2 = l \cdot \frac{K_1 C_1 + K_2 C_2}{C_0} \cdot \frac{K_3 - K_2}{K_2 K_3} \quad \ldots\ldots (2)$$

$$l_3 = l \cdot \frac{K_1 C_1 + K_2 C_2 + K_3 C_3}{K_3 C_0} \quad \ldots\ldots (3)$$

Développement par déplacement

En queue de bande, un enrichissement symétrique à celui vu au paragraphe précédent se produit. Après un certain parcours, la bande aura le profil représenté schématiquement (Fig. 2). Comme dans le cas de deux corps, on peut calculer les enrichissements en queue de bande, c'est-à-dire les longueurs l_4 et l_5 par un raisonnement analogue à celui fait précédemment. Mais ce n'est pas nécessaire, les formules précédentes étant suffisantes comme nous allons le montrer dans le cas suivant:

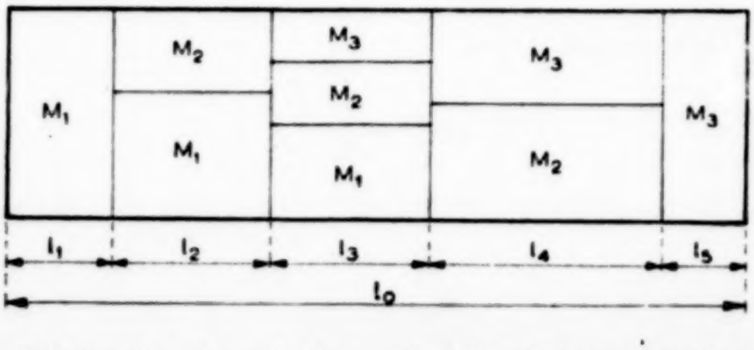

Fig. 2. Répartition des solutés pendant le déplacement d'une bande.

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Séparation de M_1 et de M_3. Ces deux ions seront séparés l'un de l'autre lorsqu'ils ne coexisteront plus dans une même bande, c'est-à-dire lorsque la bande l_3 aura disparu (Fig. 2). Pour cela il suffit d'écrire que la totalité de M_1 est accumulée dans les deux premières zones. Si la longueur totale de la bande est l_0, la quantité totale de M_1 est égale à $l_0 \cdot \frac{C_1}{C_0} C_R$.

Le bilan de cet ion est:

$$l_1 C_R + l_2 C'_{1R} = l_0 \frac{C_1}{C_0} C_R$$

l_1 et l_2 étant calculées à l'aide des relations (1) et (2). Après simplification, la relation précédente devient:

$$l = l_{1,3} = l_0 \frac{K_3}{K_3 - K_1}$$

$l_{1,3}$ représente le chemin parcouru par le front de la bande pour que M_1 et M_3 soient séparés.

Nous avons écrit que M_1 et M_3 sont séparés lorsque la totalité de M_1 est dans les deux premières bandes. On pourrait également écrire que la totalité de M_3 se répartit dans les deux dernières bandes l_4 et l_5 (Fig. 2). On aboutit à une relation identique à la relation (3). C'est pourquoi, il est inutile de calculer les longueurs l_4 et l_5.

Séparation de M_1 et de M_2. Le raisonnement est analogue à celui fait précédemment: on écrit que la totalité de M_1 est dans la bande l_1:

$$l_1 C_R = l_0 \frac{C_1}{C_0} C_R$$

l_1 étant calculée à l'aide de la relation (1). Il vient:

$$l = l_{1,2} = l_0 \frac{K_2}{K_2 - K_1}$$

Séparation de M_2 et de M_3. Ils seront séparés quand tout le soluté M_2 sera dans la bande l_2, soit:

$$l_2 C'_{2R} = l_0 \frac{C_2}{C_0} C_R$$

l_2 étant calculée à l'aide de (2). D'où:

$$l = l_{2,3} = l_0 \frac{K_3}{K_3 - K_2}$$

Sur la Fig. 3 sont représentées les différentes étapes de l'évolution d'une bande en supposant

$$\frac{K_2}{K_1} < \frac{K_3}{K_2}$$

CAS D'UN NOMBRE QUELCONQUE D'IONS

Soit une bande constituée de n ions: $M_1, M_2 - - - - - M_n$, dont les constantes d'équilibre vis-à-vis d'un autre ion M_0, sont $K_1, K_2 - - - - - K_n$ (avec $K_i < K_{i+1}$), que l'on développe par déplacement. Deux quelconques de ces ions M_i et M_k, par exemple, seront séparés, c'est-à-dire n'existeront plus simultanément dans une même bande, lorsque la bande initiale aura parcouru $\frac{K_k}{K_k - K_i}$ fois sa longeur. Autrement dit, la résolution complète de la bande en zones contenant chacune un corps pur sera obtenue après un parcours correspondant à la séparation des deux corps les plus voisins, comme s'ils étaient seuls dans la bande. Les deux ions les plus voisins M_i et M_{i+1} sont ceux pour lesquels le rapport $\frac{K_{i+1}}{K_{i+1} - K_i}$ est le plus grand, c'est-à-dire K_{i+1}/K_i le plus voisin de l'unité.

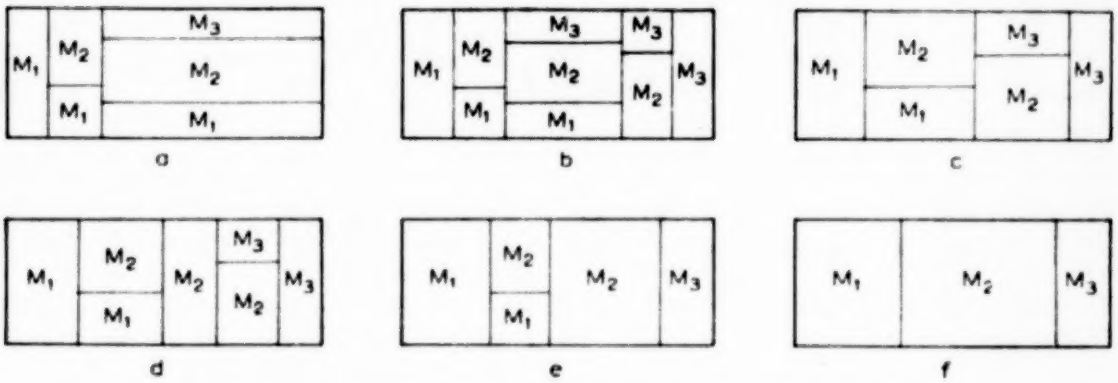

Fig. 3. Évolution d'une bande au cours d'un déplacement. Distances parcourues: a: l_0; c: $l_{1,3}$; e: $l_{2,3}$; f: $l_{1,2}$.

Nous n'indiquerons que les grandes lignes du calcul, permettant d'établir les résultats précédents, celui-ci ne présentant aucune difficulté particulière.

D'abord, si une solution contenant les solutés $M_1, M_2 - - - - - M_p$ aux concentra-

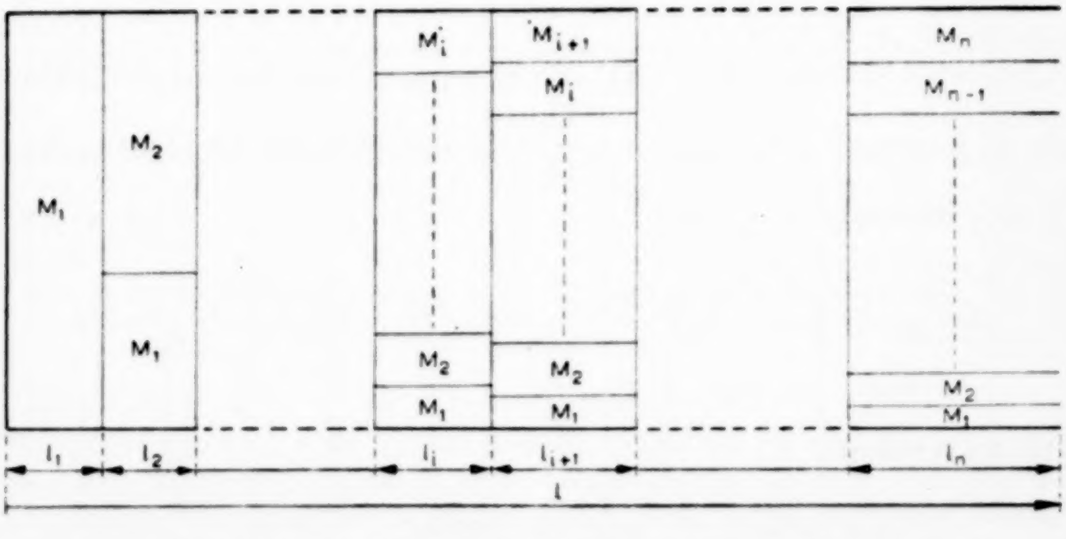

Fig. 4. Répartition des solutés dans la résine au cours d'une fixation.

tions respectives C_1, C_2 ----- C_p, est en équilibre avec une certaine quantité de résine, la concentration à l'équilibre de l'ion M_i dans la résine est:

$$C_{iR} = \frac{K_i C_i \cdot C_R}{K_1 C_1 + ----- + K_p C_p} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

D'autre part, au cours de la fixation d'une solution contenant n ions M_1, M_2, ----- M_n, il apparaît n zones[2] de longueur l_1, l_2 ----- l_n (Fig. 4) que l'on se propose de calculer. La totalité de M_n étant dans l_n, il vient:

$$l_n C_{nR} = l \frac{C_n}{C_0} C_R$$

soit

$$l_n = \frac{1}{C_0} \cdot \frac{K_1 C_1 + ----- + K_n C_n}{K_n}$$

Pour la bande l_i, c'est-à-dire la première bande dans laquelle se trouve M_i, on a:

$$l_i = \frac{1}{C_0}(K_1 C_1 + ----- + K_i C_i) \cdot \frac{K_{i+1} - K_i}{K_i \cdot K_{i+1}} \quad \ldots\ldots\ldots \quad (5)$$

Ce résultat est facilement obtenu pour l_{n-1} lorsqu'on écrit le bilan de M_{n-1}. Il suffit ensuite de démontrer que si la propriété est vraie pour l_{i+1}, elle l'est pour l_i. Pour cela il suffit dans le bilan de M_i:

$$l_i \cdot C^i_{iR} + l_{i+1} \cdot C^{i+1}_{iR} + ----- + l_n \cdot C^n_{iR} = l \frac{C_i}{C_0} C_R$$

(C^k_{iR} représentant la concentration de M_i dans la k-ième bande) de remplacer les concentrations et les longueurs par leurs valeurs obtenues respectivement à l'aide de relations analogues à (4) et (5).

Enfin les solutés M_i et M_k ($K_i < K_k$) seront séparés quand la totalité de M_i (qui pour une bande de longueur l_0 est égale à $l_0 \frac{C_i}{C_0} C_R$) sera répartie dans les bandes comprises entre l_i et l_{k-1} incluses:

$$l_i C^i_{iR} + l_{i+1} \cdot C^{i+1}_{iR} + ----- + l_{k-1} \cdot C^{k-1}_{iR} = l_0 \frac{C_i}{C_0} \cdot C_R$$

On aboutit au résultat:

$$l_{i,k} = l_0 \frac{K_k}{K_k - K_i} \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

CONDITIONS OPÉRATOIRES ET RÉSULTATS EXPÉRIMENTAUX

Nous nous sommes proposé de séparer les ions Li^+, Na^+, NH_4^+ et K^+ initialement contenus dans une même solution. Les conditions opératoires sont identiques à celles décrites précédemment[1] pour la séparation du sodium et du potassium.

Les constantes d'équilibre entre les ions H^+ et chacun des ions Li^+, Na^+, NH_4^+ et K^+ ont été déterminées expérimentalement et ont respectivement pour valeur numérique: 0.72, 1.35, 1.60 et 2.35. À l'aide de ces valeurs, il est possible de calculer la constante relative à l'équilibre entre deux des ions à séparer ainsi que la distance à faire parcourir à la bande pour que ces ions soient effectivement séparés (relation (6)). Les résultats sont rassemblés dans le tableau ci-dessous.

l/l_0 K	Li^+	Na^+	NH_4^+	K^+
Li^+		2.14	1.82	1.44
Na^+	1.88		6.4	2.35
NH_4^+	2.22	1.19		3.13
K^+	3.26	1.74	1.47	

On voit immédiatement que les ions sodium et ammonium sont les plus difficiles à séparer et que tous les ions seront répartis en zones lorsque la bande aura parcouru un chemin au moins égal à 6.4 fois sa longueur.

D'autre part, la résine étant initialement sous forme H^+ et la constante de l'équilibre entre les ions Li^+ et H^+ étant inférieure à l'unité, l'ion lithium ne peut pas déplacer l'ion H^+. C'est l'inverse qui se ferait. Cependant afin de pouvoir effectuer le déplacement, nous avons utilisé des solutions acétiques de sorte que au front de la bande on ne réalise pas l'équilibre:

$$\underset{\text{résine}}{H^+} + \underset{\text{eau}}{Li^+} \rightleftarrows \underset{\text{eau}}{H^+} + \underset{\text{résine}}{Li^+}$$

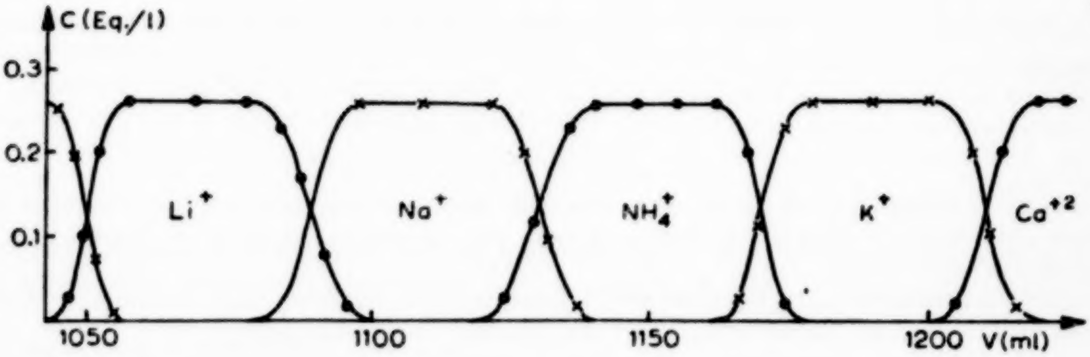

Fig. 5.

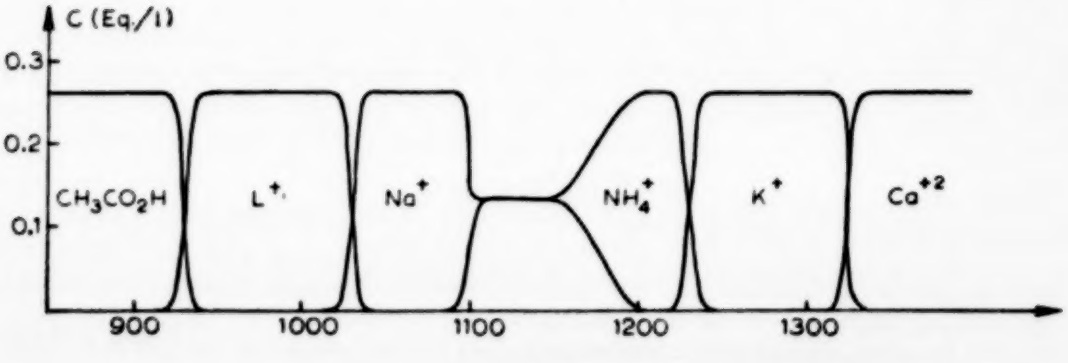

Fig. 6.

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dont la constante est égale à 0.72, mais l'équilibre:

$$\underset{\text{résine}}{H^+} + Li^+ + \underset{\text{eau}}{CH_3CO_2^-} \rightleftarrows \underset{\text{eau}}{CH_3CO_2H} + \underset{\text{résine}}{Li^+}$$

dont la constante est $0.72/K_A$, K_A étant la constante d'acidité du couple $CH_3CO_2H/CH_3CO_2^-$ qui est égale à $10^{-4.7}$. De la sorte les ions Li^+ déplacent les ions H^+ de la résine. Le développeur est constitué par une solution d'acétate de calcium $0.130M$ et dans la solution initiale les quatre ions alcalins sont dissous sous forme d'acétate, chacun à la concentration $0.065M$.

Sur la Fig. 5 sont représentées les variations des concentrations dans l'effluent après développement d'une bande de 14 cm sur une colonne de 98 cm, c'est-à-dire d'une bande ayant parcouru 7 fois sa longueur. Le chromatogramme représenté (Fig. 6) indique les variations des concentrations après développement d'une bande de 37 cm sur une colonne de 88 cm. La bande a parcouru 2.4 fois sa longueur.

INTERPRÉTATION DES RÉSULTATS EXPÉRIMENTAUX

En ce qui concerne les résultats représentés (Fig. 5), l'accord avec les prévisions théoriques est satisfaisant: les solutés sont séparés.

Dans le cas de la bande de 37 cm, qui a parcouru 2.4 fois sa longueur, d'après les valeurs de l/l_0 indiquées dans le tableau précédent, les ions Na^+ et NH_4^+ d'une part et les ions NH_4^+ et K^+ d'autre part ne devraient pas être séparés. Il en est bien ainsi pour le premier couple tandis que l'ammonium et le potassium sont séparés. Cette anomalie apparente peut être expliquée: la relation (6) précédemment établie, indique le *chemin à faire parcourir au front de la bande* pour obtenir une séparation de deux ions. Autrement dit la relation (6) indique si deux ions sont ou ne sont pas séparés à un instant donné. Or, la Fig. 6 représente les variations des concentrations à la sortie de la colonne. La queue de la bande où se trouvent les ions NH_4^+ et K^+ a donc parcouru un chemin supérieur à celui calculé (la bande a parcouru 2.4 fois sa longueur lorsque le lithium apparaît dans l'effluent).

En conclusion, les valeurs calculées à l'aide de la relation (6) permettent d'obtenir une limite supérieure de la distance à faire parcourir à la bande pour obtenir une séparation complète.

RÉSUMÉ

Dans le cas de la séparation de plusieurs corps, effectuée selon la méthode du développement par déplacement, on calcule la distance minimum à faire parcourir à la bande pour obtenir la séparation des solutés en zones.

La méthode est appliquée à la séparation des ions lithium, sodium, ammonium et potassium au moyen de la résine Dowex-50, en utilisant l'ion calcium comme développeur.

SUMMARY

In the separation of several substances by displacement development, the minimum distance is calculated that the band must travel to obtain a separation of the solutes into zones.

The method has been applied to the separation of lithium, sodium, ammonium and potassium ions on Dowex-50 resin, using calcium ions as the developer.

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Reçu le 6 janvier 1958

THE COULOMETRIC TITRATION OF BROMATE WITH CUPROUS COPPER*

by

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During the investigation of a coulometric determination of ammonia by oxidation with hypobromite[1], accurate determination of microgram quantities of bromate became necessary. If the following reaction can be made to proceed quantitatively to to the right, the problem becomes one of determining bromine.

$$6\,H^+ + BrO_3^- + 8\,Br^- \rightleftarrows 3\,Br_3^- + 3\,H_2O \qquad (1)$$

Since BUCK AND SWIFT[2] showed that small amounts of bromine can be determined by titrating with electrolytically generated cuprous copper, the applicability of a similar procedure to the determination of bromate was investigated. Such a method has the advantage that a standard reducing solution is not required.

EXPERIMENTAL

Reagents

All chemicals were reagent grade. Solutions were made by dissolving the weighed salts in distilled water. Acid solutions were made by diluting commercially available concentrated acids.

Potassium bromate (Baker and Adams C.P.) was heated for 7 h at 140° C. A 1.5-g portion was accurately weighed, dissolved in water, and diluted to 500 ml in a volumetric flask. The concentration was checked by titration[3]. Required solutions were prepared by accurate dilutions of the stock.

Apparatus

The titration apparatus and the considerations leading to the use of an indicator potential of 150 mV in most experiments were the same as those explained by ARCAND AND SWIFT[1].

Effect of bromide and cupric copper concentrations

Early in the work, there was evidence that the rate of reaction between bromine and electrolytically generated cuprous copper was dependent on the concentrations of bromide and cupric copper. The results of research now in progress indicate that the observed rate effect is caused by the formation and slow oxidation of copper and solid cuprous copper on the internal generator electrode. A series of experiments was performed in which the concentrations of bromide and cupric copper were varied. Cuprous copper was generated to titrate known quantities of bromine in these solutions. The minimum concentrations of cupric copper and bromide necessary for the rapid reduction of bromine was found to be 0.02 *VF**** and 1 *VF*, respectively.

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*** A *volume formal* (*VF*) solution contains one gram formula weight of the particular substance stated per liter of solution. A *volume molal* (*VM*) solution contains one mole of the molecular or ionic species per liter of solution.

Volatilization of bromine and oxidation of cuprous copper

Some loss of bromine and oxidation of cuprous copper might reasonably be expected, since the concentration of bromine was relatively high initially and since no effort was made to exclude air which might oxidize the cuprous copper.

The solutions used were 1 *VF* in sodium bromide, 0.02 *VF* in copper sulfate, and 1.2 *VF* in perchloric acid. A small quantity of bromine was generated so that an indicator current was obtained which was on the linear portion of the current – time curve. The exact current value was recorded. An additional 10^{-5} equivalent of bromine was then generated, after which cuprous copper was generated until the initial value of the indicator current was re-established. Under these conditions, the apparent loss of bromine amounted to 0.3 to 0.4% of the total.

When the above procedure was reversed by first generating cuprous copper and then titrating with bromine, the apparent loss of cuprous copper was about 1% of the total.

The apparent bromine loss was quite constant for a given quantity of bromine initially in the solution; therefore a titration correction was incorporated in the procedure described below.

Procedure

1. *Pre-treatment of electrodes.* The indicator electrodes were "pre-treated" before use whenever they had been out of operation for one hour or more. The 40 mm by 80 mm weighing bottle which served as a titration cell contained 10 ml of 5 *VF* sodium bromide, 1 ml of 1 *VF* copper sulfate, 5 ml of 3 *VF* perchloric acid, and 35 ml of water. The cell was mounted and bromine generated at 10 mA for about 100 sec. The polarity of the generator electrodes was reversed and cuprous copper was generated until the indicator current decreased to about 25 μA. The cell was removed, the electrodes rinsed with distilled water, the cell mounted again, and the whole procedure repeated until the indicator electrodes had a constant sensitivity, *i.e.*, the slopes of two consecutive current – time curves were the same. Two or three repetitions were generally sufficient.

2. *Establishment of initial reference current.* The titration cell contained 10.0 ml of 5 *VF* sodium bromide, 1.0 ml of 1 *VF* copper sulfate, 5.0 ml of 3 *VF* perchloric acid, and 25.0 ml of water. The cell was mounted and the "indicator potential" set at 150 mV. Bromine was generated for about 30 sec, the polarity of the generator electrodes was reversed and cuprous copper was generated until the indicator current decreased to about 40 μA. This process eliminated any reductants in the solution. When the indicator current remained stable within 0.2 to 0.3 μA for a period of 60 sec, the exact value was recorded as the *initial reference current* and was used for the calculation of the end-point correction.

3. *Determination of end-point current correction.* The cell was left in position and 10.5 ml of water was added. An amount of bromine was generated which was within 10% of that equivalent to the bromate to be titrated; the exact time of generation was recorded. Cuprous copper was generated until the indicator current decreased to about 40 μA. When the current was stable for 30 sec, the exact value was recorded along with the time of generation of cuprous copper. Generation was continued in 1.0 sec intervals until an amount of cuprous copper had been generated which was slightly in excess of the bromine previously generated. The current and time were recorded at each interval after the current was stable for 30 sec. The cell was then removed, the electrodes rinsed and the acid in the isolated compartment changed.

The end-point current correction is calculated as described in the following example:

Fig. 1 shows plots of indicator current against generation time in the vicinity of the end-point. Fig. 1a applies to a titration correction run and Fig. 1b to a titration. In Fig. 1a, i_0 is the value of the initial reference current recorded before dilution (Section 2, above), Line I is the best straight line drawn through the plotted points in the vicinity of the end-point, and t_{eq} is the known time required to generate an amount of cuprous copper equivalent to the bromine previously generated. The corresponding indicator current is designated i_{eq}. The current, i_{eq}, which corresponds to the time, t_{eq}, is subtracted from the initial indicator current, i_0, to give the end-point current correction, *C*, which will be used to calculate the end-point current for the titration.

4. *Titration.* The first part of the titration is described in Section 2, above.

The cell was left in position and 10 ml of bromate solution was pipetted into the cell. The inlet tube was washed with 0.5 ml of water. Cuprous copper was generated until the indicator current was about 40 μA. Generation was continued in 1.0-sec intervals until the indicator current was less than that calculated for the end-point. The current and time were recorded as previously described.

The end-point current and end-point time may be calculated as described in the following example:

In Fig. 1b, i_0' is the value of the initial indicator current which was recorded before the addition of the bromate sample and Line II is the best straight line drawn through the plotted points in the vicinity of the end-point. The current, i_{ep}, to be used to determine the end-point time is calculated by subtracting the end-point correction, *C*, from the initial reference current, i_0'. The generation time corresponding to i_{ep} is designated t_{ep}. Multiplication of this time by the generation rate yields the number of equivalents of bromate found in the sample.

DISCUSSION AND RESULTS

If errors are to be kept as low as 0.2 to 0.3 μg, titration correction runs must be made before and after each titration. The electrode sensitivity usually decreases slowly with the number of runs made, but becomes fairly constant after 15 or 20 runs. The average of the correction constants determined before and after a titration was found to give quite accurate results. If errors up to 1 μg can be tolerated, a series of titration correction runs can be made to establish a correction constant to be used for all subsequent titrations.

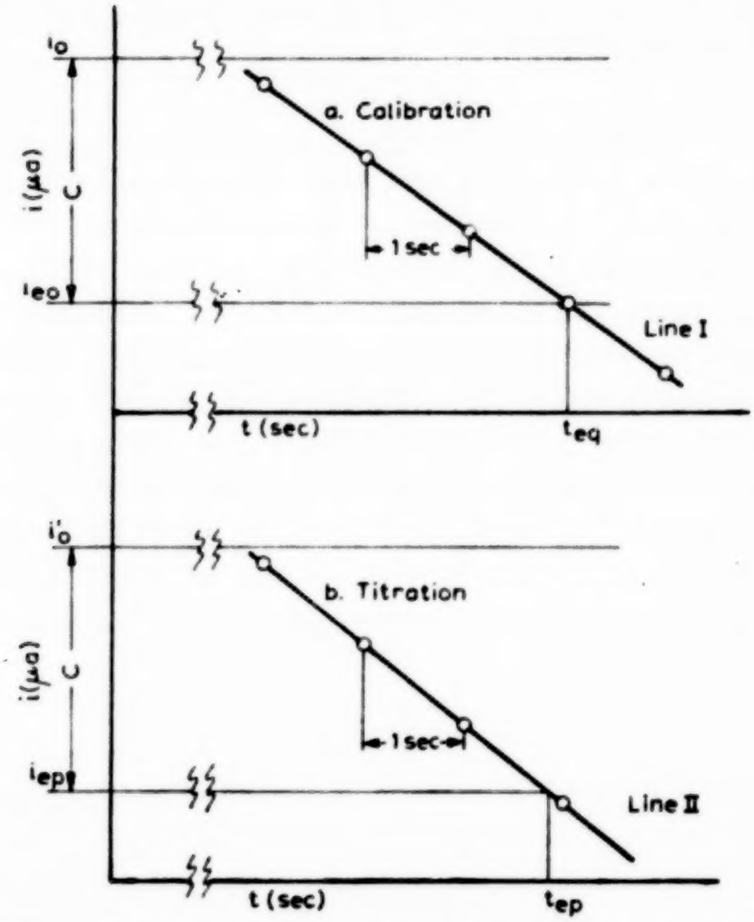

Fig. 1. Diagram for calculation of titration end-point.

Titration correction

Most coulometric procedures which use the amperometric end-point employ a blank in which the titrant is generated in the absence of the substance to be determined. A plot of current *versus* generation time is made and the time corresponding to the intercept of this line is used as a correction for the titration. The loss of bromine and the high, broad minimum in the indicator current make this type of correction impossible here. An indicator current arbitrarily selected for an end-point was found to be unsatisfactory, because the drastic treatment of the electrodes appears to prevent the reproducibility of such a point.

Effect of acid concentration

The minimum acid acid concentration is fixed by its effect on the rate of reduction of bromate; the maximum concentration is fixed by its unexplained effect in increasing the indicator current in the vicinity of its minimum. Perchloric acid was selected since, at comparable concentrations, it gave a lower minimum current than did hydrochloric acid and since results obtained with it were better than those with sulfuric acid.

Titrations were made according to the described procedure except that the perchloric acid concentration was varied. The results showed that the titration accuracy is independent of acid concentration from 0.15 to 1.2 *VF*. When the acid concentration was less than 0.15 *VF*, the reaction between bromate and bromide was so slow that cuprous copper was in excess of the bromine long before an equivalent amount had been generated. When the perchloric acid concentration was raised from 1.2 to 2.4 *VF*, the minimum indicator current increased from 24 to 43 μA. An acid concentration of 0.3 *VF* was chosen for the procedure.

Amount of bromine generated for calibration

Since the purpose of the calibration procedure is to correct for the apparent loss of bromine during the titration, the amount of bromine generated during the calibration should be close to that formed by the bromide-bromate reaction. It is therefore desirable to know how nearly equal these quantities must be in order for the calibration to be valid. Experiments were performed using the standard procedure except that the amounts of bromine generated for calibration were varied. The samples contained 238.8 μg of bromate which is equivalent to slightly more than 110 sec of generation at 10 mA. The amounts of bromine generated are indicated by the generation times. The results are shown in Table I. Errors of less than 0.3 μg were observed when the bromine was generated for 90 to 120 sec during calibration. In order to be safe, the time of generation of bromine for calibration should agree with the time of titration within 10%.

TABLE I

EFFECT OF AMOUNT OF BROMINE GENERATED FOR CALIBRATION

Titration time was 110 sec

Number of detns.	*Blank time (sec)*	*Bromate (μg)*		*Error*	
		Taken	*Found*	*(μg)*	*Standard deviation*
5	70	238.8	238.0	−0.8	±0.6
4	90	238.8	238.8	0.0	±0.1
3	120	238.9	239.2	+0.3	±0.0
4	130	238.8	239.5	+0.7	±0.7

It was found that some of the solution from the cell diffused into the isolated electrode compartment if the acid in the compartment was not changed after one or two runs. When the concentration of bromide in the compartment became sufficiently great, bromine was formed during the time cuprous copper was being generated in the cell. Near the end-point, diffusion of bromine from the isolated compartment caused the indicator current to drift and led to erratic titration results. This problem could be eliminated by use of a silver-silver chloride electrode in the isolated compartment.

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Confirmatory titrations

The results of a number of determinations performed as described in the procedure are shown in Table II. The generation rate was $1.004_5 \cdot 10^{-7}$ equivalent per sec except during the last set of titrations when it was decreased to $4.078_2 \cdot 10^{-8}$ equiv./sec in order to obtain reasonable accuracy. The accuracy of the indicator-time plot near the end-point was assured by increasing the sensitivity of the Leeds and Northrup galvanometer to $2^1/_2$ divisions per μA.

The accuracy of the method compares favorably with the amperometric method described by KOLTHOFF AND LINGANE[4]. They report errors of about 0.3% for solutions $10^{-4}N$. The average error with the coulometric method for comparable concentrations is 0.1% for 5 samples. The relative error for the small concentration of bromate is high, the average being 0.9%. However, the absolute error is about 0.2 μg, a value comparable with the absolute errors found in all of the titrations.

TABLE II

CONFIRMATORY TITRATIONS

Number of detns.	*Bromate (µg)*		*Error*	
	Taken	*Found*	*(µg)*	*Standard deviation*
2	238.8	238.8	0.0	±0.1
4	238.9	238.8	—0.1	±0.2
4	186.8	186.7	—0.1	±0.3
6	152.8	152.9	+0.1	±0.3
5[a]	18.7_0	18.5_3	-0.1_7	$\pm 0.1_2$

[a] Medium rate of generation used for this group only. High generation rate used for all other determinations.

ACKNOWLEDGEMENTS

The author wishes to thank Professor ERNEST H. SWIFT for his advice and encouragement during the experimental work and for his help in the preparation of this paper. The author is indebted to E. I. duPont de Nemours and Company for a summer research grant and to the General Electric Company for a predoctoral fellowship during the academic year 1954-1955.

The comments of Dr. ELIOT A. BUTLER and Dr. ROBERT HUFFMAN have been of value in the preparation of the manuscript.

SUMMARY

A coulometric procedure has been developed by which 18 to 240 μg quantities of bromate may be determined to within 0.3 μg. The bromate is allowed to react with bromide in an acid solution and electrolytically generated cuprous copper is used for the titration. A dual platinum electrode indicator system is used in an amperometric end-point procedure.

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Received December 12th, 1957

COULOMETRIC TITRATION OF ALUMINUM

by

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Analytical methods for the determination of a large number of the lighter elements are few in number as a result of their lack of sufficient "chemistry". Methods for the determination of aluminum fall into this category.

The chelation of aluminum with 8-quinolinol is the basis for several methods of determining aluminum. Aluminum can be precipitated as the quinolate and determined by conversion to the anhydrous quinolate or ignition to the oxide[1]. The determination of aluminum can also be completed volumetrically by bromometric titration of the quinolate with a standard solution of potassium bromate[1]. Aluminum quinolate can be extracted with chloroform and the resulting yellow-colored solution can be used as the basis for a colorimetric method[1]. The fluorescence of the quinolate can be utilized for a sensitive quantitative fluorometric method[2].

SCHWARZENBACH AND BIEDERMANN[3] determined metal ions by titrating the acid or neutral solutions of metal ions in the presence of an excess of the acid form of the chelating agent with an alkali-hydroxide solution. This paper deals with the coulometric titration of the hydrogen ions liberated on chelation of aluminum with 8-quinolinol.

Chelate formation of 8-quinolinol with low concentrations of aluminum was made more favorable by the use of ethanol solutions, which decreased the hydrolysis of aluminum quinolate. As a result, a sharper pH change at the equivalence point was obtained. Aprotic solvents, such as ethanol, greatly favor chelate formation in many cases and could be used to great advantage in utilizing chelate formation for the determination of small quantities of metal ions[4].

EXPERIMENTAL

Reagents

The aluminum stock solution was prepared from reagent-grade aluminum sulfate hydrate. The stock solution (6.657 g of $Al_2SO_4.18H_2O$ diluted to 1 l) was analyzed by taking 50-ml aliquots and precipitating the aluminum as the quinolate from a dilute acetic acid solution. The precipitate was dried to constant weight at 110°. The average of three results was $0.01040 \pm 0.0001 M$ aluminum sulfate. Known amounts of aluminum were obtained by taking 10-ml and 1-ml aliquots of 1:10 and 1:100 dilutions of the stock solution.

The supporting electrolyte solutions were prepared in 1-l quantities by dissolving appropriate amounts of sodium sulfate in slightly less than the necessary amount of water, then adding required amounts of 95% ethanol and $0.5 M$ solution of 8-quinolinol in ethanol and, finally, diluting to 1 l with water. 48% ethanol solution, $0.049 M$ in sodium sulfate and $0.0061 M$ in 8-quinolinol was used as the supporting electrolyte solution in the titration of 560-µg samples of aluminum. 59% ethanol solution saturated with sodium sulfate (slightly less than $0.05 M$) and $0.0048 M$ in 8-quinolinol was used in the titration of 56- and 5.6-µg samples of aluminum.

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Titration cell

The titration cell was a 250-ml Griffin beaker with the upper fifth cut off. The generating electrode was a 1-cm² piece of heavy platinum foil welded on to a heavy platinum wire. The auxiliary electrode compartment was a 1-cm diameter glass tube with a fine-porosity sintered glass disk in the bottom. The auxiliary electrode was a platinum electrode immersed in the supporting electrolyte solution. Nitrogen was passed through the solution to remove and to keep the solution free of carbon dioxide. A Beckman 1190-80 glass electrode and a fiber-type calomel reference electrode were used with a Beckman Model G pH-meter to measure the apparent pH of the solutions. Saturated potassium hydrogen tartrate solution, pH 3.57, was used to standardize the pH-meter. A magnetic stirrer with a teflon-coated stirring bar provided effective stirring. The titration volumes were 75 ml.

A smaller titration cell was used for the titration of 5.6-μg samples of aluminum in 20-ml solutions.

Electrical instrumentation

The constant current source is similar to that described by LINGANE[5]. The currents were determined by measuring the *iR* drop across calibrated resistors with a Leeds and Northrup Type K-2 potentiometer. Time measurements were made with a Standard Electric Time Co., Model S-10, electric stopclock.

Titration procedure

A known amount of aluminum was placed in the titration cell and diluted to 75 ml with supporting electrolyte solution. One half ml of saturated potassium chloride solution was added for titrations of 560-μg samples of aluminum. No chloride was added for the titrations of 56- and 5.6-μg samples of aluminum. The solution was decarbonated, by bubbling nitrogen through the solution for 10–15 min, after which the electrolysis was begun. The titration was allowed to proceed uninterrupted till near the equivalence point. As the equivalence point was approached, generation was carried out incrementally. pH measurements were made to define the titration curve near the equiv. p. The point of maximum slope was taken to be the equiv. p. in the titration of 560-μg samples of aluminum. A small blank correction of 1.3 ± 0.4 sec was found necessary. No blank corrections were required in titrating 56-μg samples of aluminum. The pH at the point of maximum slope was found to be 7.74 for the titration of 56-μg samples of aluminum. Titrations of two samples to this pH gave results comparable to the others. 5.6-μg samples of aluminum were titrated to pH 7.86, the pH of 20 ml of supporting electrolyte solution diluted with 1 ml of water.

TITRATION CHARACTERISTICS AND PERFORMANCE

8-Quinolinol is only very slightly soluble in water. To have a sufficient excess of 8-quinolinol in solution, aqueous ethanol solution was used. Increased ethanol concentration increased the magnitude of the potential change at the equiv. point, which is in agreement with the fact that aprotic solvents prevent solvolysis of reaction products thereby driving the reaction further toward completion. Fig. 1 shows the effect of ethanol on the titration of the hydrogen ions liberated in the formation of aluminum quinolate.

It would be expected that increase in the concentration of 8-quinolinol would favor chelate formation. However, the titration curves indicated otherwise, as can be seen in Fig. 2. 8-Quinolinol has both weak acid and weak base functions, therefore, in the presence of a large concentration of 8-quinolinol appreciable buffering occurs which flattens the titration curve near the equivalence point. By decreasing the concentration of 8-quinolinol, the buffering effect decreased and much sharper pH changes resulted. The rate of pH change at the equiv. p. is 0.08 pH units/sec in titrations of 560-μg samples of aluminum, which is sufficient for the equiv. p. to be determined within about 2 parts per thousand. The rate of pH change at the equiv. p. is about 0.02 pH units/sec in titrations of 56-μg samples of aluminum, introducing an uncertainty of a few parts per thousand. Where the rate of pH change at the equiv. p. is 0.06 pH units/10 sec, the uncertainty in titrating 5.6-μg samples of aluminum is of the order of 2%.

TABLE I

COULOMETRIC TITRATION OF ALUMINUM

Trial No.	*Aluminum taken* μg	*Aluminum found* μg	*Error* μg	*Error* %
1	561.5	561.5	0.0	0.0
2	562.1	562.6	+0.5	+0.1
3	562.1	561.0	—1.1	—0.2
4	562.1	558.8	—3.3	—0.6
5	561.8	565.6	+3.8	+0.7
6	561.8	564.8	+3.0	+0.5
7	561.5	560.7	—0.8	—0.1
8	561.5	561.8	—0.3	—0.1
9	561.5	565.8	+4.3	+0.8
10	562.1	560.2	—1.9	—0.3
11	56.21	56.46	+0.25	+0.4
12	56.18	56.06	—0.12	—0.2
13	56.18	56.21	+0.03	+0.1
14	56.15	57.21	+1.06	+1.9
15	56.15	56.18	+0.03	+0.1
16	56.18	55.53	—0.65	—1.2
17	5.61	5.45	—0.16	—2.9
18	5.61	5.58	—0.03	—0.1
19	5.61	5.15	—0.46	—8.2
20	5.61	5.47	—0.14	—2.5
21	5.61	5.29	—0.32	—5.7

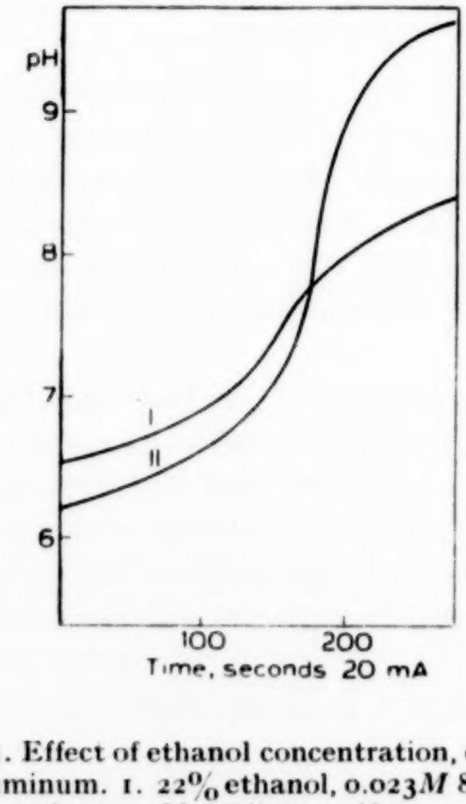

Fig. 1. Effect of ethanol concentration, 0.27 mg of aluminum. I. 22% ethanol, 0.023M 8-quinolinol and 0.045M sodium sulfate, II. 66% ethanol, 0.023M 8-quinolinol and 0.011M sodium sulfate.

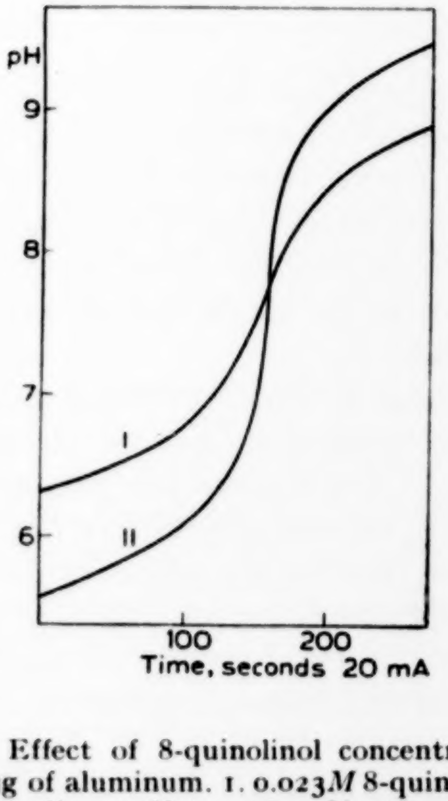

Fig. 2. Effect of 8-quinolinol concentration, 0.027 mg of aluminum. I. 0.023M 8-quinolinol, 0.046M sodium sulfate and 44% ethanol, II. 0.0058M 8-quinolinol, 0.046M sodium sulfate and 44% ethanol.

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Table I contains the results of 21 titrations of µg quantities of aluminum.

Trials 1 to 10 were performed in 75 ml of 41% ethanol solution, the concentration of 8-quinolinol was $0.0053M$, sodium sulfate $0.042M$ and potassium chloride $0.030M$. 75 ml of 56% ethanol solution, $0.0048M$ in 8-quinolinol and nearly saturated with sodium sulfate were used for trials 11 to 16. 21 ml of 56% ethanol solution, $0.0046M$ in 8-quinolinol and nearly saturated with sodium sulfate were used for trials 17 to 21.

The generating currents and titration times for the titration of 560-, 56-, and 5.6-µg samples of aluminum were *ca.* 19, 2.05, and 0.24 mA, and *ca.* 315, 290, and 296 sec, respectively.

The point of maximum slope in the titration curves was chosen as the equiv. p. for trials 1 to 14. The average equiv. p.-pH for trials 11 to 14 was found to be 7.74 pH units. Trials 15 and 16 were interpolated to such a pH.

An empirical correction factor could well be applied to the titration of 5.6-µg samples of aluminum.

Unless chloride ions were present, the titrations of 560-µg samples of aluminum gave incorrect results. The cause of this anomaly was investigated but no satisfactory explanation can be given. Current voltage curves did not indicate the presence of any reducible impurities in the solution which might be complexed by chloride ions. It was interesting to note that in the absence of chloride ions, current control was somewhat poorer. There was indication that the cell resistance was decreasing slowly during the course of the titration. No such effect was noticed in the presence of chloride ions.

Titration in chloride supporting electrolyte media was not considered, because with increasing concentration of chloride ions the titration curve flattened out at the equiv. p. due to formation of chloro complexes of aluminum. The determination of aluminum, as described, requires prior separation of ions directly reducible at a platinum cathode and also non-reducible ions which form as strong a chelate with 8-quinolinol as aluminum. Non-interfering ions are metal ions such as magnesium, the alkali and alkaline earths, which in aqueous solution form chelates with 8-quinolinol only at high pH or not at all. Fig. 3 suggests the titration of aluminum in the presence of magnesium.

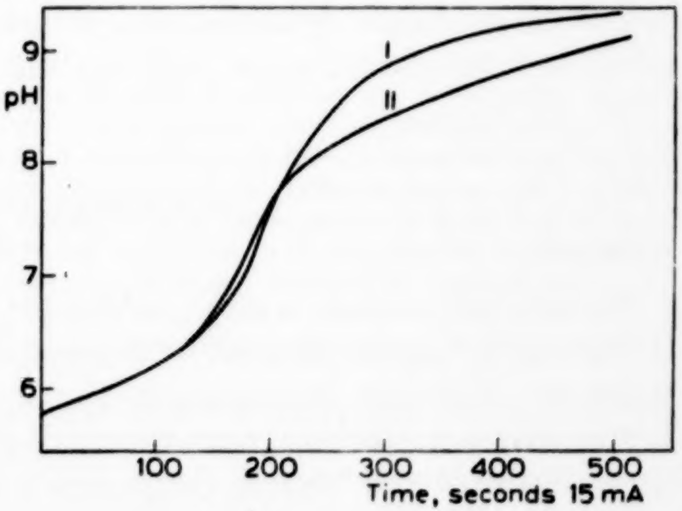

Fig. 3. Titration curves for aluminum in the presence and absence of magnesium, 0.27 mg of aluminum. I. In the absence of magnesium, II. In the presence of 0.31 mg of magnesium.

SUMMARY

An aqueous ethanol solution *ca.* $0.005M$ in 8-quinolinol and $0.04M$ in sodium sulfate can be used for the coulometric titration of small quantities of aluminum. Samples of aluminum ranging from 5 to 500 µg were successfully titrated with electrolytically generated hydroxyl ions. The end-point was detected by following the apparent pH of the solution.

References p. 276

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Received December 19th, 1957

DETERMINATION OF COPPER, LEAD, TIN AND ANTIMONY BY CONTROLLED-POTENTIAL ELECTROLYSIS

I. GENERAL METHOD OF ANALYSIS

by

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The advantages of controlled-potential electrolysis in the electrolytic separation of elements of which the deposition potentials differ only slightly, have long since been recognized. Descriptions of a number of methods in which this technique is used for the successive deposition of some of these elements from the same solution, have already appeared in print.

In this paper a method is presented which permits the electro-deposition in successive stages, of copper, lead, tin, and antimony, and a report on the results obtained on analysing synthetic solutions of these metals is given. A comparison with existing methods will be made in a forthcoming paper when the application of this particular method to the analysis of bronzes and brasses will be discussed. In following papers descriptions will be given of the application of the method to the analysis of some alloys and of the successive determination of nickel, zinc and aluminium possibly present in solutions from which copper, lead, tin and antimony have been removed.

DESCRIPTION OF THE METHOD

Principle

Tartaric and succinic acids are added to the hydrochloric solution of the alloy which is then made almost neutral with ammonia and electrolysed – in the presence of hydrazine as anodic depolarizer and at a controlled cathodic potential – to deposit copper first and then lead; from the residual solution, acidified with hydrochloric acid, tin is deposited and then, in the presence of hydriodic acid as reducer, antimony.

Reagents (Merck, pro analysi)

Concentrated hydrochloric acid, sp.gr. 1.19.
Diluted hydrochloric acid (1 + 1).
Concentrated ammonia, sp.gr. 0.91.
30% hydrogen peroxide.

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Tartaric acid.
Succinic acid.
Sulfamic acid.
Hydrazine dihydrochloride.
Potassium iodide.
Washing solution: distilled water containing one drop of ammonia per litre.

Electrolytic equipment

The determination of Cu–Pb–Sn–Sb is carried out with a controlled-potential electrolytic apparatus with manual or automatic adjustment; the anode and the cathode, cylindrical and of the gauze type, have the following dimensions: height = 50 mm, diameter = 35 and 53 mm respectively. They are fastened to a rod along which they may be raised or lowered; the rod is attached to a magnetic stirrer. The calomel electrode is also movable along the rod of a three-legged support.

The following directions refer to the platinum electrodes described above. Electrodes of other sizes will probably require distinctly different electrolysis conditions, especially at the beginning of copper deposition when this metal forms a spongy deposit on the edges of the cathode if the initial current density is too high.

Dissolving the sample

This can be carried out either in a 400-ml tall-form electrolysis beaker covered with a large-size watch glass or in a 250–300 ml flask with ground neck in which a condenser is inserted.

Though this second technique might at first seem rather laborious, it is actually more simple because it does not call for any particular care and is a guarentee against possible losses of tin or antimony through evaporation or of copper through drag.

Treat 1 g of alloy with 10–12 ml diluted HCl and 2 ml H_2O_2. Allow to react, then heat on a sand bath or moderate flame and, if required, continue to add H_2O_2, at intervals and little by little using a pipette, until the sample is completely dissolved (if dissolution is performed in a flask, H_2O_2 is added from the top of the condenser).

When dissolution is complete, add 1–2 more drops of H_2O_2 and boil for 10–15 min. If the alloy was dissolved in a beaker, it is advisable to dilute to 40–50 ml with distilled water before boiling. If any cloudiness develops due to antimony or tin, this is easily eliminated by adding a few drops of concentrated HCl and heating.

Allow to cool down to 40–50°; in another beaker containing a small amount of distilled water dissolve 5 g of tartaric acid and pour into the sample solution, letting the liquid flow along the walls of the beaker or of the condenser.

Wash the watch glass and beaker walls (or condenser walls) with distilled water. If during the dissolution process some sulfur has separated, filter by washing with warm distilled water and collect the filtrate in a 400-ml tall-form electrolysis beaker. Otherwise, transfer the flask contents to a 400-ml tall-form electrolysis beaker; if dissolution had already been carried out in a beaker, no transfer will be required.

Determination of copper

Add 3 g of succinic acid and 2 g of hydrazine dihydrochloride to the solution; if necessary, dilute to about 200 ml and dissolve the added substances by stirring the liquid magnetically.

It is not necessary to wait until the succinic acid is completely dissolved, because it will do so during the subsequent addition of ammonia. While keeping the liquid under agitation, add concentrated ammonia to pH 5. The best way of adding ammonia is to use a large size dropping tube so that at the beginning of neutralization, 3–4 refills will suffice to add the amount of ammonia required, while at the end of this phase — indicated by the bluish coloration of copper salts —, only a few drops at a time should be added.

A too high pH can be corrected with diluted HCl, provided a pH of about 6 has not been exceeded during neutralization.

The narrow-range pH-test papers do not generally give an exact indication of the pH; however they may be used for checking once and for all the colour that the test papers assume at the pH value indicated by a pH-meter. This observation holds also for the electrolysis described below.

Immerse the electrodes and the saturated calomel electrode (S.C.E.) (as close as possible to the cathode, but not in contact with it, and with the tip reaching half way down the outer surface of the cathode) and deposit the copper at a cathode potential of —0.35 V *vs.* S.C.E.; often, however, if the copper percentage is high, the initial current intensity should not exceed 1.4 to 1.5 A in order to prevent an excessively fast, and hence spongy, deposition; as the electrolysis progresses, the cathode potential decreases and when —0.35 V *vs.* S.C.E. is reached, it will maintain this constant minimal value. When current intensity has dropped to 0.1–0.05 A bring the cathode potential to —0.40 V *vs.* S.C.E. and keep it at this level throughout the rest of the electrolysis. After the current intensity has remained constant for 10–15 min, electrolysis is finished; generally, the intensity drops to 0.01 A and often even below that; the deposition of 0.6 to 0.9 g of copper will take 45–60 min.

After electrolysis, lift the calomel electrode and wash it with the washing solution. Next, lift the electrodes without breaking the circuit and wash them immediately with a fine stream of washing solution directed around the top edge of the cathode from a washing bottle, so that the liquid will fall into the electrolysis beaker: two, or at the most three uniform sprayings around the top edge of the cathode will complete the washing.

Proceed in the same way to wash the anode. Remove the cathode, wash with alcohol and ether, dry at 100–110° for 2–3 min and weigh.

Keep the copper-plated cathode for the subsequent deposition of lead.

Determination of lead

Under magnetic stirring adjust the pH of the solution to 5.4–5.5 by adding concentrated ammonia: generally, 15–25 drops of ammonia will be sufficient, the exact amount being dependent on the case in question. If necessary, correct the pH value with dilute HCl and re-check accurately.

Replace the copper-plated cathode, gently stir the liquid, close the circuit, immerse the electrodes and the calomel electrode, and bring the cathode potential to —0.60 V *vs.* S.C.E.

When the lead content exceeds 70–80 mg, the initial current intensity should not exceed 0.15 A to obtain a good deposit; when most of the lead has deposited, gradually bring the potential from —0.60 to —0.65 V *vs.* S.C.E.

After 30–35 min the current intensity falls to a constant minimal value; wait for another 15 min and then wash the calomel electrode, the anode and cathode as described for copper, using the same washing solution. Afterwards remove the cathode, wash in alcohol and ether, dry at 100–110° for 2–3 min and weigh.

Dissolve the deposit on the cathode with diluted HNO_3 (1 + 1).

Determination of tin

Add 20 ml of concentrated HCl to the solution and deposit tin on the smooth platinum cathode.

After immersion of the electrodes and of the calomel electrode in the gently agitated solution, close the circuit and feed an 0.8–1 A current. A vigorous evolution of gas results and after 2–3 min the cathode potential will reach —0.60 V *vs.* S.C.E. Keep the cathode potential constant at this value; after a few minutes gas evolution will almost cease. At this point, add about 0.5–0.7 g of sulfamic acid to the solution, stir rather vigorously and bring the cathode potential to —0.65 V *vs.* S.C.E. When the current intensity has dropped to 0.10–0.15 A add about 0.2–0.3 g more of the sulfamic acid and bring the cathode potential to —0.70 V *vs.* S.C.E. If the amount of tin present is less than 20–30 mg, it will suffice to add 0.2–0.3 g of sulfamic acid after the evolution of gas at —0.60 V *vs.* S.C.E., and immediately start the electrolysis at —0.70 V *vs.* S.C.E.

After the intensity has dropped to a constant minimal value (generally 0.05–0.15 A, according to the case in question) wait a further 15 min, then wash, dry and weigh in the usual manner.

The electrolysis will take from 40–50 min.

Clean the cathode with a lukewarm diluted HNO_3 (1 + 1) solution containing tartaric acid; then wash with distilled water and clean again with a lukewarm diluted HCl (1 + 1) solution.

Determination of antimony

Heat the solution on a hot plate to incipient boiling and transfer it to the electrolytic apparatus. Antimony is also deposited directly on the platinum.

Stir the solution gently, immerse the electrodes and the calomel electrode, close the circuit and feed a current of 0.4–0.5 A into the solution. Immediately add some potassium iodide crystals and, also immediately, adjust the cathode potential to —0.45 V *vs.* S.C.E.; maintain this value throughout the electrolysis. Continue to add potassium iodide at regular intervals of a few minutes, until the solution takes on a straw-yellow colour.

Continue the electrolysis until the current intensity remains constant, wait for 15 min and wash, dry and weigh in the usual manner.

The electrolysis will take from 30–40 min.

Antimony deposits in a blackish form and will only adhere to the electrode if it is present in an amount not exceeding 15–20 mg; it adheres better on a sand-blasted gauze.

Clean the cathode with a lukewarm diluted HNO_3 (1 + 1) solution containing tartaric acid.

DISCUSSION

In order to dissolve copper alloys in hydrochloric acid an oxidant must be added, such as potassium chlorate[1], nitric acid[2,3], or hydrogen peroxide[4]; for the electrolysis discussed here, hydrogen peroxide was preferred because it does not introduce any ions into the solution and can be almost entirely eliminated by boiling. As will be seen later, antimony must of necessity be completely oxidized to the maximum valence and this is achieved by means of the chlorine derived from the oxidation of hydrochloric acid; it follows that an excess of oxidant is certainly favourable in the dissolution process, though it might disturb or impede the complete deposition of tin during the electrolysis. On account of what has been said above, it is the author's opinion that hydrogen peroxide is to be preferred as the oxidant, because it can easily be eliminated after dissolution.

The electrolysis of the metals discussed here, in a slightly acid tartrate solution has the advantage that lead can be separated from tin and that an optimum copper deposit is obtained, as has been demonstrated by LINGANE AND JONES[2,3]; but, whereas those authors used sodium hydroxide to neutralize the acid solution resulting after dissolution, I prefer ammonia.

The method of AYLWARD AND BRYSON[5] – in which the acid solution is neutralized with ammonia to prevent lead losses during washings – suggested to the author that by depositing the lead from a solution almost entirely neutralized with ammonia, it could be possible to avoid these losses without having to resort to a rather troublesome procedure (as neutralization without breaking the electric circuit certainly would be), which might even interfere with the analysis if ammonia were inadvertently added in excess.

This hypothesis has been experimentally confirmed. It was, however, found that, though beneficial in the deposition of lead, neutralization with ammonia has two drawbacks in the electrolysis of copper when this is deposited before lead: (1) the necessity of adding ammonia during electrolysis, because the buffer capacity of the solution is not sufficient to keep the pH constant throughout the deposition, and (2) incomplete deposition of copper that is sometimes obtained.

The first drawback is due to the hydrogen ions resulting from the anodic oxidation of hydrazine[2,3], while the cause for the second is not very clear; the author believes that on neutralization a slightly alkaline pH is at times present in a few spots of the liquid and for brief intervals. Under these conditions the reaction of Fehling will take place in a solution containing cupric ions, tartrates and a reducer like hydrazine, and result in the formation of cuprous hydroxide[6].

However, no precipitate is observed and the copper remaining in the solution is not even deposited during the successive electrolysis of lead and tin. The cuprous hydroxide is probably present in colloidal form. In any case, both of the said drawbacks can be eliminated by adding succinic acid, the dissociation constant values of which[7] ($pK_1 = 4.18$ and $pK_2 = 5.6$) have already induced LINGANE AND JONES to use this acid for a similar purpose[2,3]. However, if in spite of the presence of succinic acid the neutralization of the solution by ammonia reaches a pH higher than about 6, the results obtained are often low, even if no precipitate is formed and if the pH is corrected to the right value of about 5 before copper electrolysis is started.

If silver and bismuth are present, they are also deposited together with copper; however, some tests run with 0.4 g of copper and 0.1 g of bismuth have shown that the former is deposited at —0.26 V *vs.* S.C.E. and the latter at —0.40 to —0.45 V *vs.* S.C.E. For this reason, this method should also make possible the deposition of bismuth intermediate between that of copper and lead.

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Deposition of lead is inhibited by the presence of aluminium, but in order to obtain a complete deposition of lead it is sufficient to work at a more highly negative potential, in accordance with the instructions that will be outlined when the applications of the method are dealt with.

Nickel, if present in large quantities, partly co-deposits with lead if the cathode potential exceeds —0.65 V *vs.* S.C.E. (see Table III, A); on the other hand, once lead has been deposited, nickel deposition will be negligible even if the cathode potential is brought to —1 V *vs.* S.C.E.

The reasons why aluminium and nickel behave as they do are still obscure. Probably, some complexes are formed in the solution, which should account for a more negative potential being required to deposit lead, as well as for the preferential deposition of a lead-nickel alloy instead of pure lead.

LINGANE AND JONES[2,3] obtained deposition of tin on the copper- and lead-coated cathode, after acidification and addition of hydrazine to the solution remaining after removal of copper and lead. Copper and lead have a higher overvoltage than platinum with respect to hydrogen, which makes them more convenient, but when following this procedure, the author has often found 1.5–2.5 mg less tin than the theoretical amount present. Better results were obtained by using sulfamic acid; nevertheless, results were frequently low and the author observed that this occurred mostly when lead had deposited on the copper-coated cathode in such a way that small but numerous areas

TABLE I

ANALYSES OF SYNTHETIC SOLUTIONS

Other elements present: Ni = 50 mg; Mn = 50 mg; Zn = 50 mg; Fe = 25 mg.
(All weights in grams)

Expt. No.	*Cu*		*Pb*		*Sn*		*Sb*	
	weighed	*found*	*weighed*	*found*	*weighed*	*found*	*weighed*	*found*
1	0.7368	0.7375	0.0219	0.0212	0.1190	0.1186	—	—
2	0.8178	0.8177	0.0493	0.0491	0.1141	0.1138	—	—
3	0.7628	0.7622	0.0561	0.0556	0.0914	0.0912	—	—
4	0.8208	0.8206	0.0466	0.0462	0.1994	0.1999	—	—
5	0.7452	0.7452	0.0991	0.0995	0.1157	0.1160	0.0075	0.0071
6	0.7564	0.7563	0.0998	0.0998	0.1764	0.1762	0.0047	0.0044
7	0.8336	0.8339	0.0686	0.0684	0.1216	0.1221	0.0088	0.0082
8	0.8081	0.8075	0.0625	0.0632	0.0846	0.0845	0.0042	0.0036
9	0.8291	0.8291	0.0517	0.0515	0.0464	0.0456	0.0055	0.0051
10	0.7976	0.7970	0.0498	0.0495	0.1372	0.1365	0.0056	0.0053
11	0.8048	0.8044	0.0234	0.0236	0.0796	0.0789	0.0030	0.0026
12	0.8054	0.8061	0.0174	0.0176	0.1570	0.1565	0.0018	0.0013
13	0.8037	0.8034	0.0173	0.0170	0.1100	0.1093	0.0067	0.0062
14	0.8494	0.8490	0.0122	0.0128	0.0881	0.0871	0.0042	0.0040
15	0.8596	0.8590	0.0099	0.0097	0.0651	0.0653	0.0060	0.0057
16	0.7628	0.7624	0.0079	0.0082	0.0617	0.0607	0.0061	0.0059
17	0.8016	0.8018	0.0064	0.0059	0.1853	0.1848	0.0074	0.0069
18	0.8079	0.8074	0.0057	0.0063	0.1436	0.1436	0.0028	0.0021
19	0.8008	0.8004	0.0061	0.0056	0.1259	0.1258	0.0038	0.0033
20	0.8009	0.8010	0.0056	0.0050	0.1251	0.1249	0.0027	0.0024
21	0.8622	0.8621	0.0044	0.0042	0.0736	0.0730	0.0060	0.0054
22	0.7999	0.7995	0.0069	0.0067	0.1067	0.1074	0.0078	0.0068
23	0.7988	0.7983	0.0052	0.0052	0.1460	0.1464	0.0026	0.0024
24	0.8085	0.8079	0.0039	0.0037	0.0566	0.0566	0.0044	0.0045

of the copper deposit were left uncovered, on account of the adhesion of gaseous bubbles. Not even tin will deposit on these areas. The author then attributed the incomplete deposition of tin to washing losses caused by the formation of voltaic couples in the areas of contact of the three metals, and to eliminate this trouble, the deposition of tin directly on the platinum was adopted. Initially, a strong evolution of hydrogen on the platinum surface is noticed, but this can be greatly diminished if the gauze is copper- or lead-plated.

Then, as the tin deposits, evolution of gas diminishes progressively until it almost disappears. But if the platinum surface is wrinkled and slightly dark owing to recent sand-blasting of the gauze, evolution of gas will continue throughout the electrolysis and the deposition of tin will not be complete (see Table III, B). This is evidently a case of variation in the overvoltage of hydrogen, depending on the aspect of the platinum surface. From the solution remaining after removal of copper, lead and tin, heated to 80–90°, it is possible to precipitate antimony with hydrogen sulphide, but it can also be deposited by electrolysis after reducing its valence to three. To this end, hydriodic acid was used, as it reduces antimonic compounds when hot[6]. Tervalent antimony deposits in a blackish form that is not quite compact and only slightly adherent, as already observed by LASSIEUR[1]; the method outlined here is suitable only for low antimony contents as are encountered, for instance, in bronzes. In fact, amounts larger than 15–20 mg easily peel off while washing; a far better adherence is obtained on sand-blasted gauzes.

TABLE II

ANALYSES OF SYNTHETIC SOLUTIONS

(All weights in grams)

Expt. No.	*Cu*		*Pb*		*Sn*		*Sb*	
	weighed	*found*	*weighed*	*found*	*weighed*	*found*	*weighed*	*found*
1	0.8086	0.8079	0.1030	0.1031	0.0855	0.0851	0.0056	0.0053
2	0.7869	0.7879	0.1012	0.1010	0.1196	0.1201	0.0044	0.0040
3	0.7942	0.7951	0.0954	0.0946	0.0985	0.0983	0.0047	0.0043
4	0.8067	0.8066	0.0719	0.0723	0.1047	0.1041	0.0040	0.0038
5	0.7987	0.7986	0.0663	0.0665	0.0960	0.0952	0.0042	0.0044
6	0.8081	0.8085	0.0496	0.0490	0.1354	0.1345	0.0041	0.0038
7	0.8511	0.8509	0.0173	0.0168	0.0802	0.0800	0.0053	0.0052
8	0.8575	0.8573	0.0117	0.0110	0.1217	0.1219	0.0043	0.0037
9	0.8544	0.8550	0.0082	0.0076	0.1441	0.1436	0.0039	0.0040
10	0.8533	0.8530	0.0077	0.0074	0.0967	0.0975	0.0043	0.0039
11	0.8210	0.8210	0.0043	0.0043	0.1151	0.1143	0.0026	0.0020
12	0.8189	0.8195	0.0044	0.0038	0.0972	0.0965	0.0020	0.0019
13	0.8044	0.8045	0.0265	0.0261	0.0978	0.0979	0.0027	0.0028
14	0.8174	0.8177	0.0045	0.0046	0.1600	0.1599	0.0058	0.0051
15	0.8462	0.8460	0.0932	0.0932	0.1555	0.1552	0.0055	0.0046
16	0.7985	0.7981	0.0079	0.0074	0.1488	0.1489	0.0053	0.0046
17	0.8379	0.8380	0.0945	0.0948	0.1168	0.1165	0.0092	0.0088

Other elements present:
Expts. 1–12 : Ni, Zn, Mn 100 mg each; Fe 50 mg.
Expt. 13 : Ni, Zn, Mn 50 mg each; Fe 25 mg; Al 5 mg.
Expts. 14–15 : Ni, Zn, Mn 50 mg each; Fe 25 mg; Al 10 mg.
Expts. 16–17 : Ni, Zn, Mn 100 mg each; Fe 50 mg; Al 10 mg.

TABLE III

UNSATISFACTORY DETERMINATIONS AND CAUSES OF ERRORS

(See DISCUSSION)

	Cu	*Pb*	*Sn*	*Sb*
A. Cathode potential is too negative, lower than —0.65 V *vs.* S.C.E., and maintained for a few minutes during lead deposition: results are too high on account of the partial co-deposition of nickel.				
1. Weighed g	0.7476	0.0168	0.1592	—
Found g	0.7475	0.0184	0.1586	
2. Weighed g	0.7647	0.0983	0.1584	0.0061
Found g	0.7647	0.1000	0.1577	0.0059
3. Weighed g	0.7997	0.0113	0.0624	0.0093
Found g	0.7995	0.0136	0.0621	0.0088
4. Weighed g	0.8051	0.0252	0.1517	0.0046
Found g	0.8048	0.0268	0.1513	0.0044
B. Deposition of tin on a gauze cathode that has recently been sand-blasted: strong evolution of gas throughout electrolysis and incomplete deposition of tin.				
5. Weighed g	0.7646	0.0517	0.1115	0.0044
Found g	0.7643	0.0513	0.1079	0.0040
C. Dissolution with insufficient oxidation: partial co-deposition of Sb and Sn.				
6. Weighed g	0.7578	0.0050	0.0547	0.0049
Found g	0.7576	0.0046	0.0578	0.0010
D. Where hydrogen peroxide has not been completely eliminated, depositions are complete (2 drops of 10% H_2O_2 added to the solution, after sample dissolution and cooling).				
7. Weighed g	0.8067	0.0224	0.1460	0.0042
Found g	0.8066	0.0228	0.1452	0.0038

Other elements present:
Expt. No. 4 : Ni, Zn, Mn 100 mg each; Fe 50 mg.
Other experiments : Ni, Zn, Mn 50 mg each; Fe 25 mg.

As indicated in Expt. No. 6, Table III, antimony co-deposits with tin. It should first of all be pointed out that during the dissolution of this test sample, the addition of hydrogen peroxide was interrupted when some undissolved metal chips were still present. The solution was kept hot until complete dissolution had taken place and then analysed in accordance with the method described. Evidently, one of two things had occurred during dissolution: either the entire amount of antimony present was not oxidized, or the dissolved antimony was partially reduced by the metal chips still undissolved when the addition of hydrogen peroxide was stopped.

From the results of this experiment and some others not referred to here, the author came to the conclusion that only tervalent antimony co-deposits with tin, that is to say, co-deposition only takes place if during dissolution oxidation has been incomplete.

The author believes that also in the methods of LINGANE AND JONES[2,3] and of AYLWARD AND BRYSON[5], the partial co-deposition of antimony with tin or with lead is to be ascribed to incomplete oxidation during dissolution. Oxidation of antimony occurs by the action of chlorine and, from this point of view, potassium chlorate is the oxidant to be preferred; however, hydrogen peroxide – though less efficient in producing chlorine – does not carry any ions into the solution and can be eliminated more easily.

The author also believes that when copper is deposited from a hydrochloric solution at room temperature, antimony – if present – will co-deposit with copper only if it is tervalent; in this case, however, it still remains to be investigated whether a partial reduction of antimony does or does not occur during electrolysis. Some experiments carried out by the author in this connection have not yet given a final answer, and it is his intention to continue the tests. On the other hand, when dissolving metals in the presence of an oxidant (in however small amount) – as in the case of nitric acid in LINGANE's method[2,8] – it will hardly be possible entirely to avoid oxidizing the antimony and, hence, a complete co-deposition of antimony with copper will be difficult to accomplish.

DETERMINATIONS IN SYNTHETIC SOLUTIONS

After the necessary preliminary tests with solutions containing some of the elements to be examined, some systematic tests were run, the results of which have been partly quoted in Tables I, II and III.

The solutions to be analyzed were obtained by dissolving weighed amounts of copper, lead, tin and antimony in hydrochloric acid and hydrogen peroxide, in accordance with the method described. Also aluminium, when present, was weighed and dissolved together with the other metals. To the solution thus obtained were added, 50 or 100 ml respectively, of a solution containing, per l, 1 g each of zinc, nickel, and manganese and 0.5 g of iron; this solution was prepared by dissolving the necessary amounts of pure metals in 40 ml of hydrochloric acid (1 + 1) with the aid of hydrogen peroxide, then boiling and bringing the volume to 1 l with distilled water.

As may be noted in Tables I and II, the results are undoubtedly satisfactory and the errors that might occur are in the order of not more than ± 1 mg, *i.e.*, 0.1% if the weight of the sample to be analysed is 1 g. In Table III some of the causes for the errors mentioned in discussing the method are presented.

ACKNOWLEDGEMENTS

It is a pleasure to thank Dr. A. ZAZZARONI, the Director of the Fiat Laboratories for his encouragement and kind permission to publish this paper, Dr. S. BERTOLDI for stimulating discussions in the course of this work and Mr. P. GIACCONE for his enthusiastic co-operation.

SUMMARY

A controlled-potential electrolysis method is described, by means of which it is possible to deposit copper, lead, tin and antimony from the same solution in successive stages. The behaviour of each metal during deposition as well as the best working conditions are discussed. The determinations are not affected by moderate amounts of Ni, Zn, Mn, Fe, Al.

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Received January 15th, 1958

POLAROGRAPHIC DETERMINATION OF SEMICARBAZONES*

by

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A reliable analytical method for the determination of organic carbonyl compounds in polluted and industrial atmospheres in the parts per hundred million range has not been available. The bisulfite method studied by GOLDMAN AND YOGADA[1] and reviewed by REYNOLDS AND IRWIN[2] is satisfactory for gas-phase sampling of formaldehyde but generally unsatisfactory for higher aldehydes and ketones. The oxime method described by SIGGIA[3] requires that condensed samples be used, and long reaction times are necessary in some cases. The 2,4-dinitrophenylhydrazone chromatographic method, described by ROBERTS AND GREEN[4] and others, requires a reaction mixture so strongly acid that certain carbonyl compounds may undergo side reactions. Inasmuch as these commonly used analytical methods are not particularly well suited to the determination of aldehydes and ketones as atmosphere contaminants, it was decided that other methods of analysis should be investigated.

The kinetics and equilibria of semicarbazone formation have been studied by CONANT AND BARLETT[5]. They showed that the rate of semicarbazone formation is dependent on the concentration and nature of all acids present and that rates of semicarbazone formation were most rapid at a pH of 4 to 5. This same pH region is also satisfactory from the standpoint of equilibria, since a pH of 4 or greater is desirable. Thus, it was assumed that the use of the non-volatile semicarbazone derivative of carbonyl compounds formed in an acetic acid-acetate buffer solution would be satisfactory for quantitative absorption of carbonyl compounds from air samples both from the standpoints of equilibria and rates of semicarbazone formation. A stable derivative having been found, it was then necessary to develop a rapid, accurate method of measuring the amount of semicarbazone formed in the reaction of semicarbazide with aldehydes and ketones.

It was found in the present investigation that semicarbazones of aldehydes and ketones give well defined polarographic waves in buffered solutions in the pH range of 4 to 5. Consequently, aliphatic ketones can be determined quantitatively by this method, whereas the simple ketones themselves are not polarographically active. Semicarbazones are non-volatile compounds, making it possible to sample polluted air for several volatile carbonyl compounds without appreciable losses by bubbling it through a simple liquid scrubber fitted with a sintered glass bubbler. Sampling studies should be extended to include a larger variety of compounds. In most cases, the carbonyl compound-semicarbazone equilibrium is displaced well toward complete conversion to the semicarbazone. Since the buffer solution used in the sampling procedure is satisfactory as a supporting electrolyte for the polarographic determination of semicarbazones, the sampling and analysis steps can be carried out using a single solution.

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* Presented at the XVth International Congress of Pure and Applied Chemistry, Lisbon, Sept. 1956.

PROCEDURE AND APPARATUS

The polarographic determinations were made with a Sargent Model XXI recording polarograph. An "H" type cell was used with provisions for flushing out the portion of the salt bridge adjacent to the dropping mercury electrode compartment with saturated potassium chloride solution between determinations. The reference cell was a saturated calomel electrode (S.C.E.). The value of $m^{2/3}t^{1/6}$ in the voltage range of —1.0 to —1.4 V, *vs.* S.C.E., was 1.80 in all cases.

An aqueous supporting electrolyte solution that was 0.1 *M* each in acetic acid, sodium acetate, sodium chloride, and semicarbazide, and that was 0.0016% in Triton X-100, a polarographic maximum suppressor, was used throughout for the gas phase sampling experiments and also for the polarographic determinations, unless otherwise specified.

A simple one-stage liquid scrubber, with a medium-pore-size sintered-glass disc in the bottom, was used in the gas phase sampling experiments. The sampler had a volume of 5 ml and was charged with 2 ml of semicarbazide solution. Known carbonyl compound–air mixtures were prepared by evaporating a small volume of a dilute benzene solution of a known carbonyl compound in the appropriate volume of air. The aldehyde– or ketone–air mixture was then drawn through the scrubber charged with semicarbazide solution, at a rate of 50 to 100 ml/min. The concentration of semicarbazone in the scrubber solution was then determined polarographically.

The procedure for sampling contaminated air or automobile exhaust gases was essentially the same as that used for known carbonyl compound–air mixtures. Here, the gaseous sample was drawn through the scrubber for a measured period of time. The volume of gas was then calculated on the basis of flow rate, time, pressure, and temperature. The concentration of semicarbazone in the bubbler solution was then determined polarographically.

The inorganic reagents were all C.P. grade and the carbonyl compounds were used as received from the various chemical supply houses without further purification. In all cases, only freshly opened organic reagents were used.

Tygon tubing and silicone stopcock lubricant were found to give interferences when incorporated in the apparatus. Although gum rubber tubing was satisfactory for connections in the gas handling system, an all-glass apparatus is desirable. In addition, most laboratory glassware had adsorbed impurities that give interferences. These can be removed by rinsing the glassware with semicarbazide reagent before use.

RESULTS AND DISCUSSIONS

Semicarbazone polarograms

Typical polarograms of 0.1 m*M* solutions of several aldehyde and ketone semicarbazones are given in Fig. 1. Fig. 2 shows a polarogram for a mixture of formaldehyde, acetaldehyde, and acetone semicarbazones at pH 4.6, in the absence of a maximum suppressor. There are three distinct waves, with the formaldehyde wave first, followed by the acetaldehyde wave, and finally the acetone wave. Thus, under ideal conditions it is possible to make quantitative determinations of mixtures of these materials on the basis of a single polarogram, since the potential at which reduction takes place is characteristic of the type of compound. The method should be generally suitable for the analysis of binary mixtures if the halfwave potentials are separated by at least 0.2 V.

Calibration data, including half-wave potentials, diffusion current constants, $i_d/Cm^{2/3}t^{1/6}$, and the concentration ranges studied are given in Table I. The diffusion current constants, and consequently the relative polarographic sensitivities, are nearly the same for all of the compounds listed in Table I. Thus, the total diffusion current at —1.4 V *vs.* S.C.E. may be used as a measure of the total amount of carbonyl compounds present in the sample. The polarograms for crotonaldehyde semicarbazone given in Fig. 3 show a linear increase in wave height with increasing concentration. These solutions contained no maximum suppressor, since crotonaldehyde semicarbazone

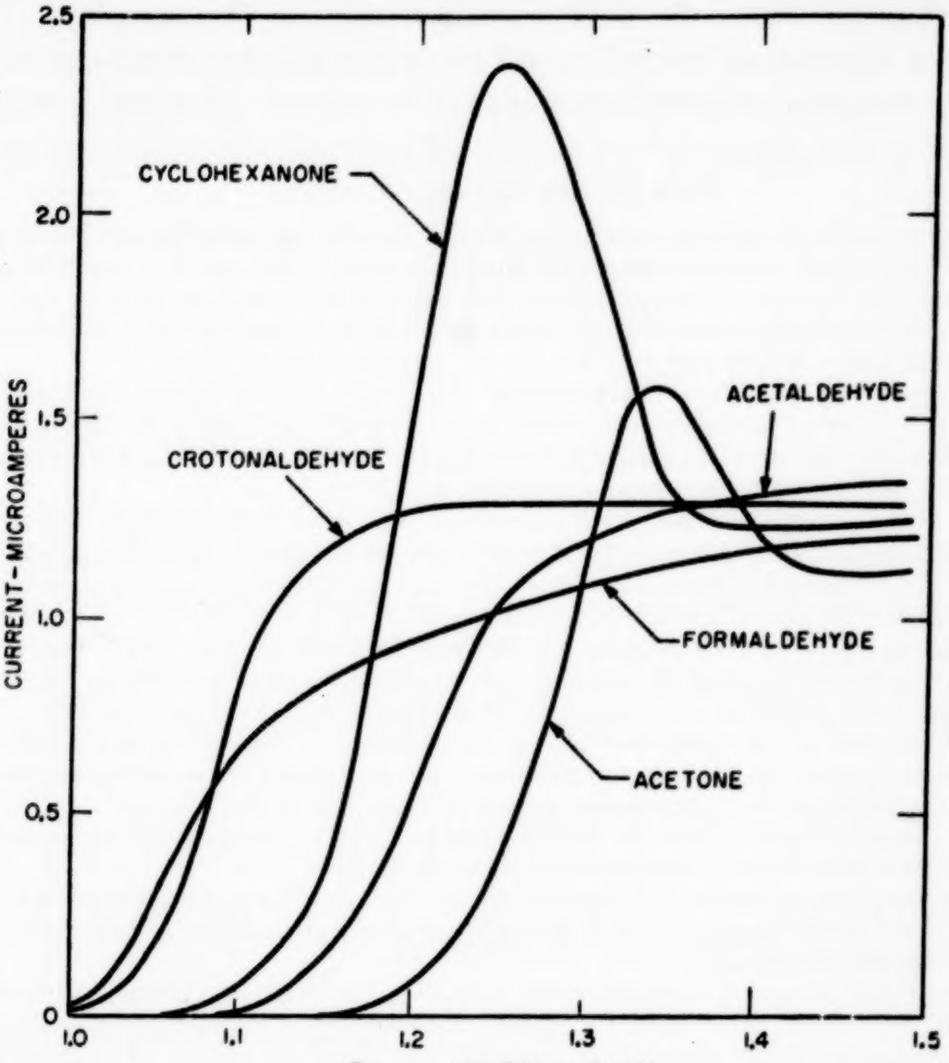

Fig. 1. Semicarbazone polarograms. Note: In each case the triton X-100 concentration was 0.0016%.

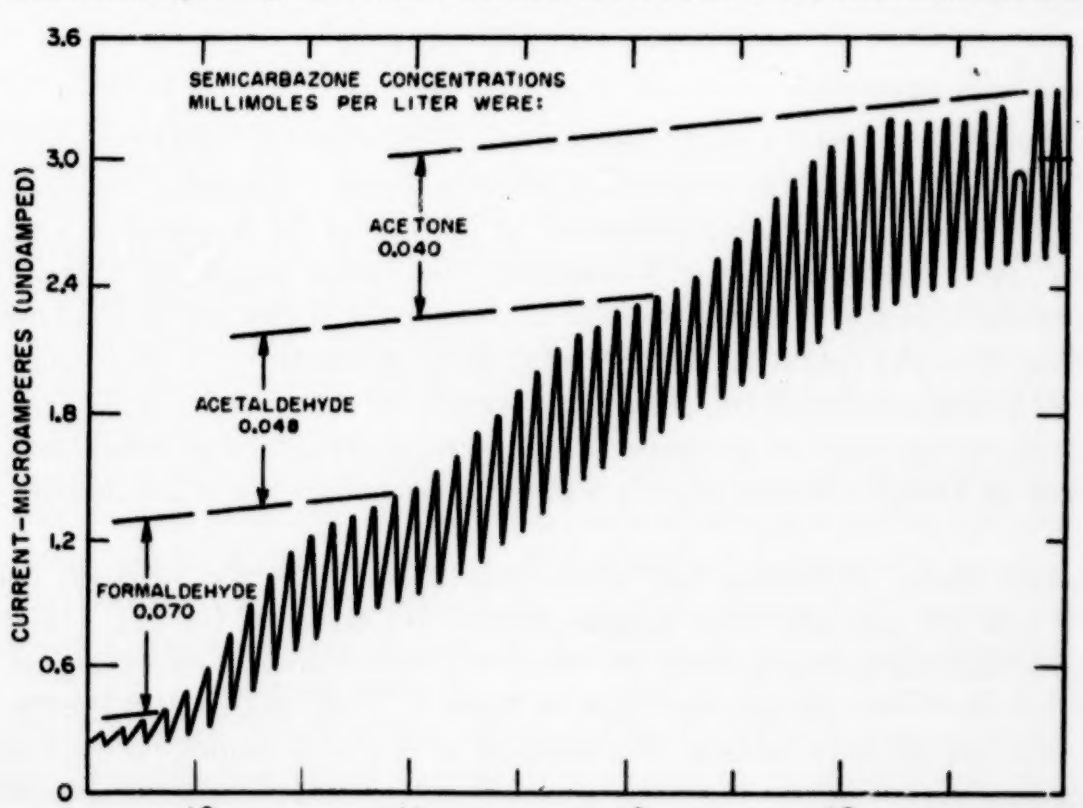

Fig. 2. Polarogram of semicarbazone mixture.

gives a normal wave in the acetate-acetic acid buffer solution. The half-wave potential does not shift with increasing concentrations for crotonaldehyde nor for any of the other compounds studied. Thus, a polarographic semicarbazone determination is excellent as a means of quantitative analysis of solutions of known carbonyl compounds. Aldehyde semicarbazone half-wave potentials are generally at less negative values than are ketone half-wave potentials. The type of carbonyl compound in an unknown sample can thus be determined from the half-wave potential, and the amount from the wave height.

In the absence of a maximum suppressor, most of the semicarbazones show maxima. These maxima may be suppressed adequately for quantitative analysis in most cases

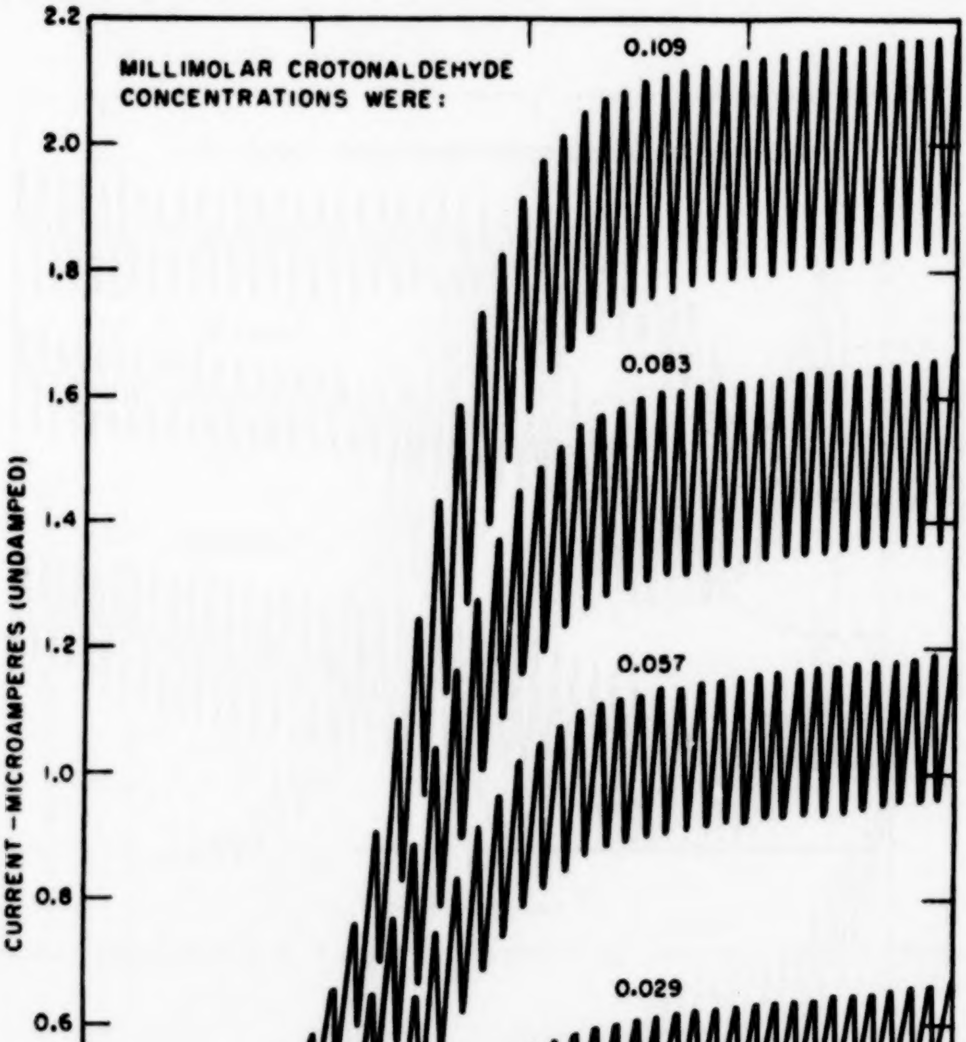

Fig. 3. Crotonaldehyde semicarbazone polarograms.

by 0.0016% Triton X-100. Higher concentrations of Triton X-100 cause serious distortion of the aldehyde semicarbazone waves. Fig. 4 shows the effect of increasing concentrations of Triton X-100 on the formaldehyde semicarbazone waves. It is apparent that Triton X-100 concentrations far below the critical micelle concentrations (0.0022%)[6] decrease the wave height. The ketone semicarbazone maxima are extremely large and some of the aldehyde semicarbazone waves are irregular in the absence of a maximum suppressor. The effect of varying concentrations of Triton X-100 on the acetone semicarbazone wave is shown in Fig. 5. The maximum is suppressed completely at 0.0039% Triton X-100; the wave, however, is also somewhat distorted. It was decided, as a result of this type of study for each of the compounds reported in this paper, that 0.0016% Triton X-100 was satisfactory as a maximum suppressor.

The reduction mechanism probably involves three or four equivalents per mole of

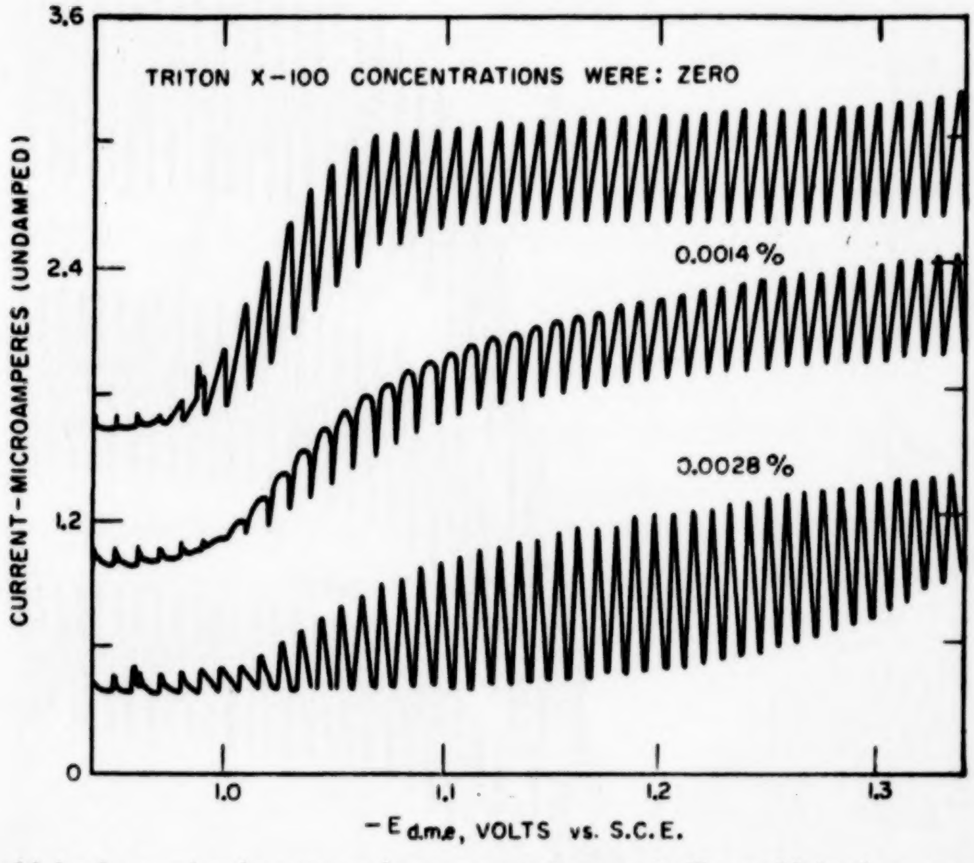

Fig. 4. Formaldehyde semicarbazone polarograms at pH 4.6. Formaldehyde concentration was 0.08 m*M* in each case.

TABLE I

POLAROGRAPHIC CALIBRATION DATA FOR SEMICARBAZONES

Semicarbazone	*Concentration range, $10^5 M$*	*Diffusion current constant $(i_d/Cm^{2/3}t^{1/6})$*	*$E^{1/2}$ Volts vs. S.C.E.*
Formaldehyde	2–18	6.9	1.05
Acetaldehyde	2–25	7.1	1.16
Butyraldehyde	2–8	7.0	1.11
Acetone	1–8	6.8	1.3
Cyclohexanone	1–21	6.2	1.2
Acrolein	4–36	6.8	0.99
Crotonaldehyde	2–11	6.7	1.06
Methyl isobutyl ketone	3–20	4	1.3

semicarbazone. Based on the shapes of the polarographic waves, however, the reduction mechanisms, assuming reversible electrode reactions, apparently involve one equivalent per mole of semicarbazone. If this is correct, the semicarbazone diffusion coefficients must be exceptionally large compared with those for the parent carbonyl compounds. A value of $1.3 \cdot 10^{-4}$ is obtained for the diffusion coefficient, D, in the Ilkovic equation for a diffusion current constant of 7 and an n-value of 1. It is more likely that n is 3 or 4, giving diffusion coefficients of approximately 10^{-5}, which are comparable with those of the parent carbonyl compounds.

Similar polarographic waves were observed for acetone, acetaldehyde and formaldehyde semicarbazones in a 0.1M formic acid-sodium formate buffer with a pH of 3.7. This fact together with the observation that the diffusion currents were found to be

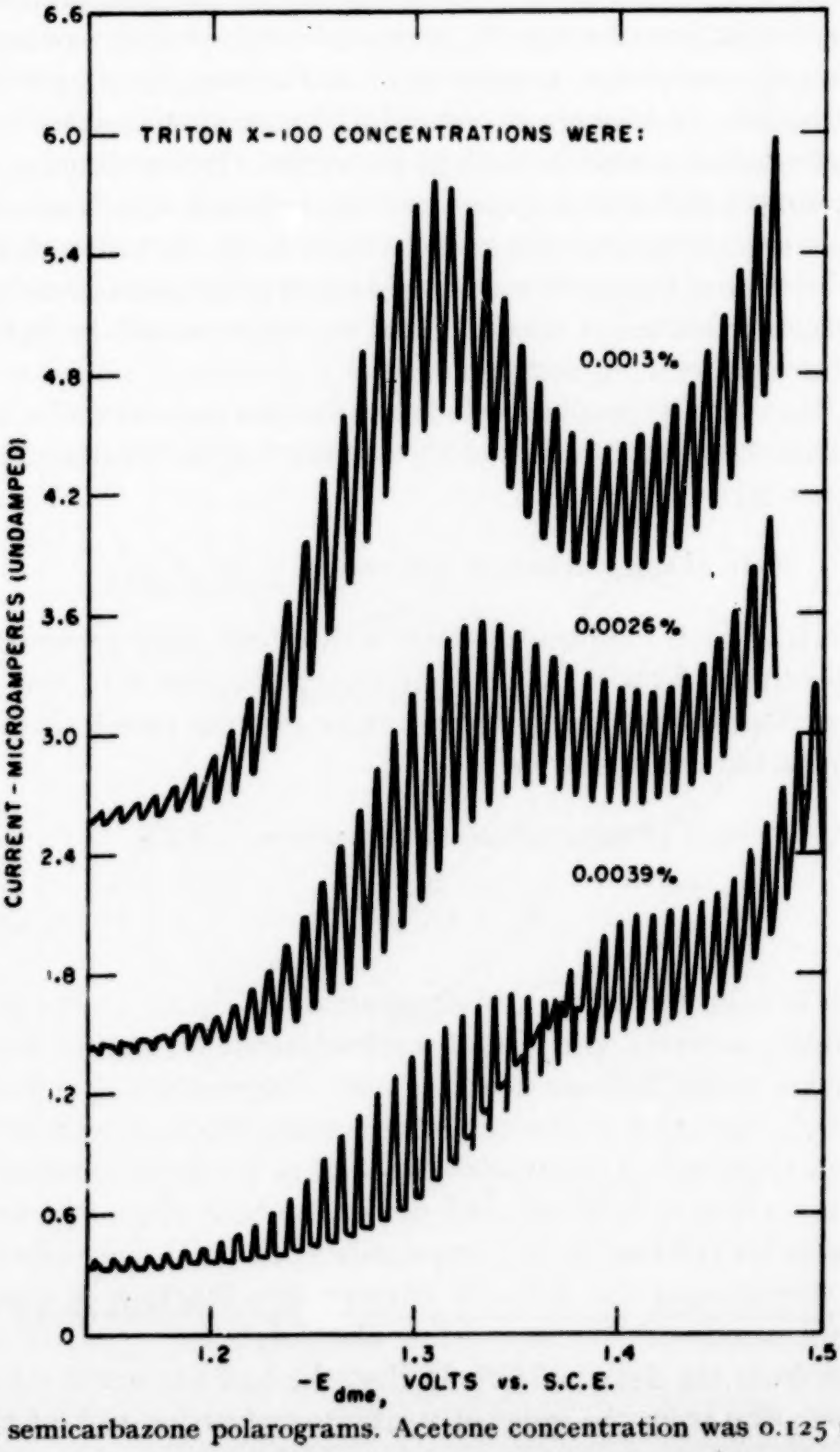

Fig. 5. Acetone semicarbazone polarograms. Acetone concentration was 0.125 mM in each case.

directly proportional to the semicarbazone concentrations indicates that the polarographic waves represent true reductions rather than catalytic deposition of hydrogen.

Semicarbazone diffusion current constants are all large, making the method considerably more sensitive than straight polarographic determination of aldehydes with diffusion current constants in the range of 2 to 3. Saturated ketones are not readily determinable polarographically. However, the corresponding semicarbazones give polarographic waves that are quite satisfactory for quantitative analysis.

Gas phase carbonyl compound determination

The polarographic semicarbazone method outlined in the present paper should be applicable for carbonyl compound determination in industrial areas or wherever appreciable amounts of organic matter are volatilized. The method has specificity, since it depends on the formation of a specific derivative followed by a polarographic analysis that is unusually sensitive to semicarbazones. Further, the supporting electrolyte contains semicarbazide, a relatively strong reducing agent which would reduce a number of possible interfering materials, such as peroxides. On standing for several hours, for example, hydrogen peroxide is quantitatively reduced. The limit of detection of the polarographic determination of semicarbazones is on the order of $5 \cdot 10^{-6} M$.

From a consideration of the reaction rates of carbonyl compounds and semicarbazide in acetic acid–acetate buffers it was felt that the rates would be sufficiently great to give efficient gas-phase sampling.

CONANT AND BARTLETT's[5] results showed that the rate expression for semicarbazone in a buffer solution containing acetic acid, acetate ion, semicarbazide and acetone or furfural is given by

$$\text{Rate of semicarbazone formation} = kC_A C_S C_C \quad \dots\dots\dots \quad (1)$$

where C_A, C_S and C_C are the concentration of acetic acid, semicarbazide and carbonyl compound, respectively. Now if the concentrations of acetic acid and semicarbazide are much greater than that of the carbonyl compound, the pseudo-first-order rate expression for semicarbazone formation is

$$\text{Rate of semicarbazone formation} = k_1 C_C \quad \dots\dots\dots\dots \quad (2)$$

where

$$k_1 = k C_A C_S \quad \dots\dots\dots\dots\dots\dots \quad (3)$$

This equation is valid for acetic acid concentrations up to $0.1 M$. At higher acetic acid concentrations, however, the rate of semicarbazone formation does not increase in direct proportion to the increase in acetic acid concentration. For furfural, the rate increased only by a factor of 2 for a ten-fold increase in acetic acid concentration.

Table II gives a summary of the available rate data for semicarbazone formation in a solution that is $0.1 M$ each in acetic acid, sodium acetate, semicarbazide, and sodium chloride. The rates for the first three compounds in Table II were determined polarographically by determining the diffusion current as a function of time after mixing the carbonyl compound with the supporting electrolyte.

It can be seen from the data in Table II that the half-life in the $0.1 M$ acetic acid–semicarbazide solution is on the order of a minute or less for each of the compounds

TABLE II

RATES OF SEMICARBAZONE FORMATION

Carbonyl compound	k_1 *(min⁻¹)*	*Initial carbonyl compound concentration ($10^5 M$)*
Methyl isobutyl ketone	0.7	19.5
Crotonaldehyde	1.3	2.88
Butyraldehyde	2.5	4.58
Acetone	4[a]	—
Furfural	10[a]	—

[a] Calculated from CONANT AND BARTLETT's data[5].

tested. It should be possible to increase the reaction rates somewhat by using higher semicarbazide and acetic acid concentrations. This would be necessary if these rates are found to be too slow for efficient gas-phase sampling with a simple scrubber.

Typical data for the determination of aldehydes and ketones at concentrations of a few parts per million in synthetic mixtures in air are given in Table III. In each case, an air sample containing a measured amount of carbonyl compound was scrubbed through the semicarbazide-supporting electrolyte in a bubbler type liquid scrubber with a fritted glass disc in the bottom. The carbonyl compound, converted to the corresponding semicarbazone in the solution, was then determined polarographically. In all cases studied, the carbonyl compounds were quantitatively absorbed by the semicarbazide solution. Since only a limited number of compounds have been tested,

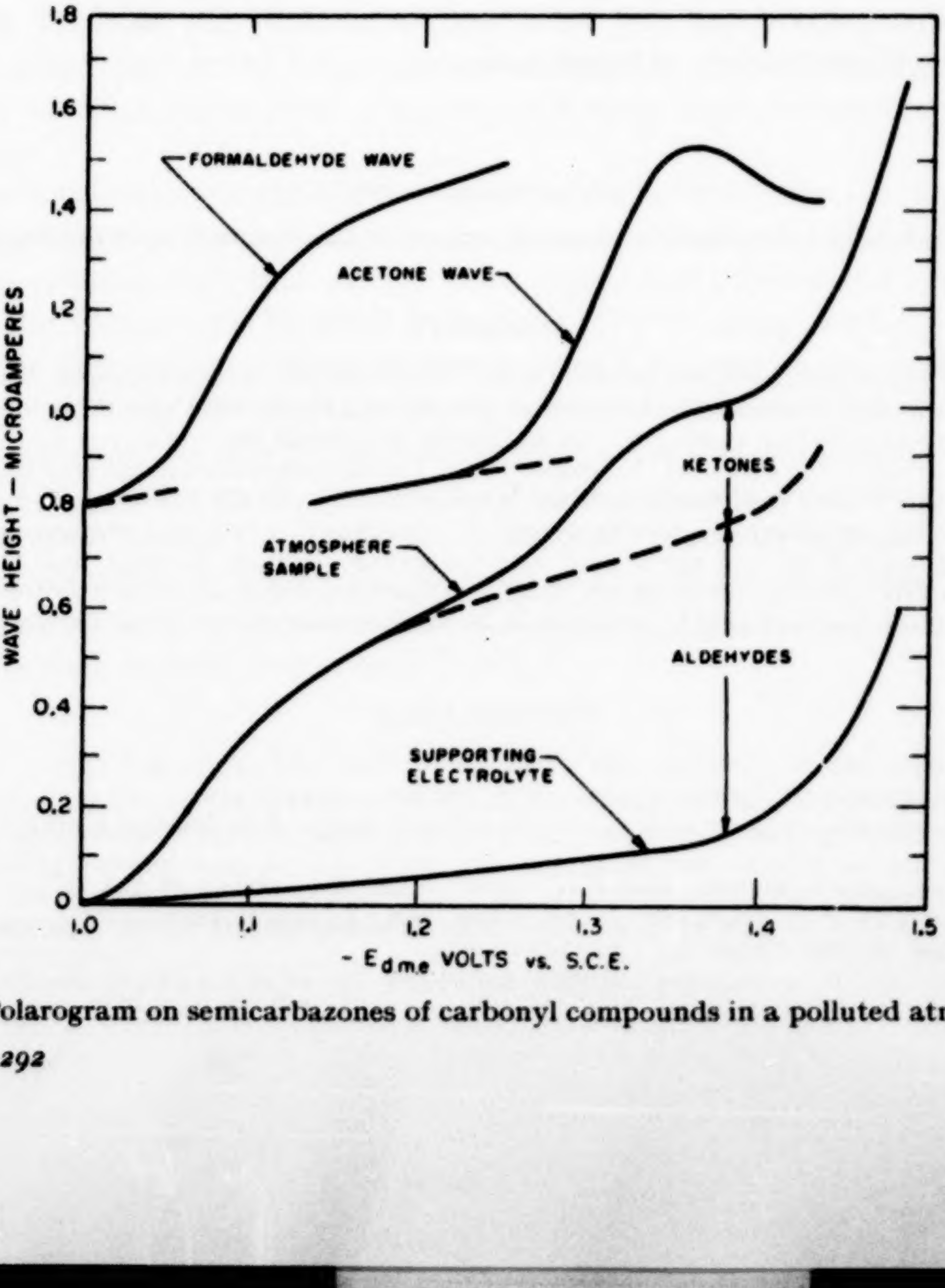

Fig. 6. Polarogram on semicarbazones of carbonyl compounds in a polluted atmosphere.

TABLE III

GAS PHASE CARBONYL COMPOUND DETERMINATION

Carbonyl compound	*μg*		*P.p.m. by volume in the gas phase*
	taken	*found*	
Acetone	2.0	2.0	1.0
Acetaldehyde	2.0	2.0	1.3
Cyclohexanone	8.0	8.1	2.4
Crotonaldehyde	8.0	7.9	3.3

further gas phase sampling experiments should be conducted to test the scrubbing efficiency of this solution for other compounds.

Although the purpose of the present investigation was to develop a method for the determination of carbonyl compounds, the results of a determination on a polluted atmosphere sample is also included as an example of possible applications of the method. In this case, the atmosphere was sampled for 2 h by scrubbing air at the rate of 2 l/h directly through the semicarbazide-supporting electrolyte solution. The polarogram of the resulting solution is given in Fig. 6. For comparison, polarograms for formaldehyde and acetone are also included in Fig. 6. Assuming the carbonyl compounds in the atmosphere to be mainly acetone and formaldehyde, this determination indicated 0.4 p.p.m. by volume of aldehydes calculated as formaldehyde, and 0.2 p.p.m. by volume of ketones calculated as acetone. Aldehydes, such as crotonaldehyde, give semicarbazone waves at the same potential as formaldehyde, and saturated ketones behave like acetone. These data therefore represent total aldehyde and ketone concentrations. The method has also been used successfully for aldehyde and ketone determinations in automobile exhaust gases.

ACKNOWLEDGEMENT

The author grafefully acknowledges financial support of this research from the American Petroleum Institute.

SUMMARY

Acetone, methyl isobutyl ketone, acetaldehyde, formaldehyde, cyclohexanone, butyraldehyde, crotonaldehyde, and acrolein semicarbazones all give polarographic waves suitable for quantitative analysis in an acetate buffer at pH 4.6. The half-wave potentials are —1.3, —1.3, —1.16, —1.05, —1.2, —1.11, —1.06, —0.99 V *vs.* S.C.E., respectively, for the compounds listed above. The diffusion current constants of these compounds average approximately 7 in the concentration range of 10^{-2} to 10^{-1} mM, giving an extremely sensitive method of carbonyl compound analysis. A supporting electrolyte that is 0.1 M each in acetic acid, sodium acetate, sodium chloride, and semicarbazide, and 0.0016% in Triton X-100, is satisfactory both for polarographic analysis and for the quantitative absorption of acetone, acetaldehyde, cyclohexanone, and crotonaldehyde from air samples by means of a scrubber.

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Received December 27th, 1957

THE POLAROGRAPHIC DETERMINATION OF ALUMINIUM*

V. THE OSCILLOGRAPHIC POLAROGRAPHY OF ALUMINIUM IN CALCIUM CHLORIDE SOLUTION

by

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INTRODUCTION

In previous papers in this series the polarography of aluminium has been reviewed[1] and studies of the Solochrome Violet R.S. method of WILLARD AND DEAN[2] have been reported. The development of a method for the determination of microgram amounts of aluminium in beryllium has been described[3] and some fundamental studies of the aluminium-azo dye reaction have been presented and discussed[4].

The Solochrome Violet R.S. method has great sensitivity, but it relies upon the modification, by aluminium, of the reduction step produced by the dye. The upper limit of aluminium which can be determined therefore depends upon the solubility of the dye. The solubility of Solochrome Violet R.S. limits the permissible concentration of aluminium in the final solution to about 8 μg/ml. Considerable dilution of the sample solution is, therefore, often required and a high standard of reagent purity is necessary.

In order to provide a method better suited to the determination of larger concentrations of aluminium it was decided to investigate the direct polarography of aluminium in chloride solution. This had already been abandoned after initial experiments[1], in favour of the Solochrome Violet R.S. method. The literature already mentioned in part I of this series[1] was therefore re-examined and, in addition, the work of ISHIBASHI AND FUJINAGA[5] and HIBINO, HAYASHI AND SHINAGAWA[6] was studied.

Calcium chloride was selected as base electrolyte for this work since, during investigations of the polarographic behaviour of some elements in concentrated calcium chloride solution[7] using the linear-sweep cathode ray polarograph[8,9] well-defined peaks, later shown to be due to the presence of aluminium, were observed. Previous experience with this medium also indicated that some of the more serious interferences, by elements such as iron, might be avoided.

EXPERIMENTAL

All polarography was carried out at 25° on the linear-sweep cathode ray polarograph and *versus* the mercury pool anode. The instrument employed was RANDLES-type single sweep polarograph[8,9], having a voltage sweep rate of 0.3 V/sec. All potentials are quoted on the European sign convention. On this convention the potential of the saturated calomel electrode (S.C.E.) has been taken as + 0.246 V *versus* the normal hydrogen electrode (N.H.E.).

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Preliminary experiments

Initial experiments were made with a base electrolyte of $5M$ calcium chloride, as this was the concentration present in the solution which yielded the aluminium peaks mentioned above. The solution was prepared by dissolving AnalaR calcium carbonate in hydrochloric acid. Before use, electrolysis at a stirred mercury cathode for $2^{1}/_{2}$ h at —1.6 to —1.8 V *versus* S.C.E. was found to be necessary to remove metallic impurities more noble than aluminium.

Portions of this solution, each of 10 ml, were evaporated to 8 ml and aliquots equivalent to 500 μg of aluminium (as sulphate) were added. Sufficient $0.1N$ hydrochloric acid was then added to give a final pH of about 4 and the solutions were made up to 10 ml in graduated flasks. The final pH values were determined on 1-ml portions of these solutions after tenfold dilution as previously recommended[7].

Polarography *versus* the silver–silver chloride electrode, after deoxygenation, failed to give reproducible results. It was, however, shown that, as previously predicted[1], the pH range for the satisfactory direct polarography of aluminium is very narrow. The aluminium was precipitated at pH 4.6 and at pH values significantly less than 4 the aluminium peak suffered interference from the hydrogen reduction.

These results, and those from similar series of solutions, also revealed that the aluminium wave obtained was not a single peak and that the shape of the wave altered if the cathode ray polarograph was allowed to sweep repeatedly for several min. A badly-formed prewave appeared during this period and increased in size with time. The peak moved from an initial —1.57 V to —1.52 V. The initial and final wave shapes are shown in Fig. 1. During these changes the cathode ray polarograph remained fully in synchronisation with the dropping mercury electrode and it was shown that the phenomenon was not caused by the entry of oxygen. Further, the phenomenon was found to be independent of the electrode and cathode ray polarograph employed.

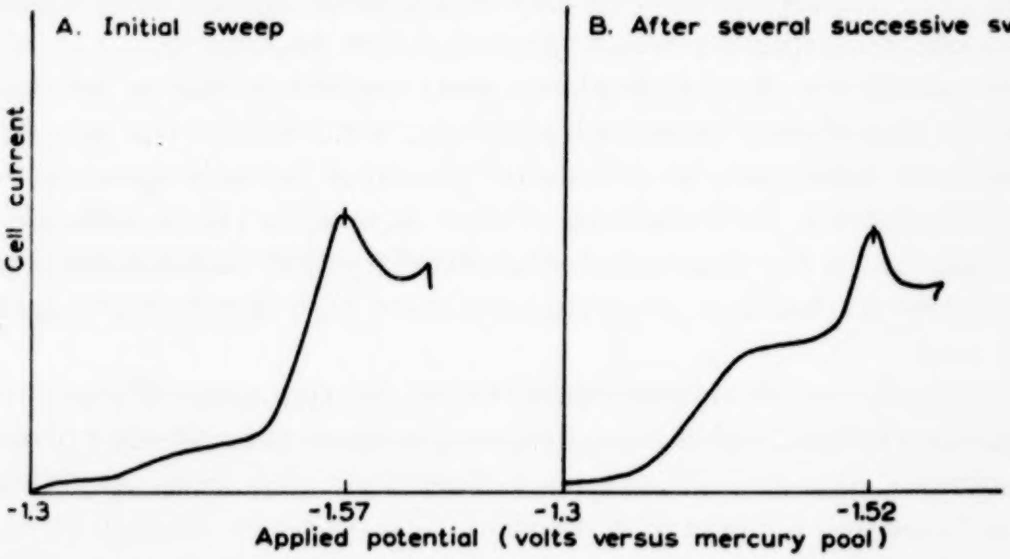

Fig. 1. Aluminium in $5M$ calcium chloride (Cathode ray polarograph) pH = 4.

Experiments were next carried out with other concentrations of base electrolyte, with the object of finding more stable conditions for the reduction.

A series of solutions was prepared exactly as described above, except that the concentration of the calcium chloride varied from $5M$ to $0.1M$. Aliquots were deoxygenated and polarographed.

The results showed that stable polarograms were obtained when the concentration of calcium chloride was less than $0.3M$. Above this figure the phenomenon already mentioned occurred and, in addition, an interfering wave at —1.8 V was observed, which increased in size with increasing base electrolyte concentration.

Attempts were made to remove this interference by standing the solutions in boiling water for varying lengths of time. This treatment reduced the height of the interfering wave and increased that of the normal aluminium peak. The former never completely disappeared, however, and the change was complete after 20 min, further heating having no effect.

Since no advantage appeared to be gained by the use of concentrated base electrolyte solutions all further experiments were made in $0.1M$ calcium chloride, as electrolytic purification of the solution was unnecessary at this low concentration.

A series of solutions was again prepared as above, but all were $0.1M$ with respect to calcium chloride and 50 μg/ml with respect to aluminium. The pH of these solutions ranged from 3.9 to 4.5.

Deoxygenation and polarography yielded very interesting results. Solutions of pH greater than 4.3 gave a wave identical with that of the base electrolyte alone, indicating the precipitation of the aluminium. In the other solutions a peak due to aluminium was obtained at —1.64 V *versus* the mercury pool, provided that the start potential control of the polarograph was set to start the voltage sweep at —1.40 V. If, however, the start potential was reset to —1.42 V the wave rapidly changed in shape over successive sweeps, until it was undistinguishable from the wave due to base electrolyte. On returning to the original start potential setting this condition persisted until the aluminium peak was restored by tapping the dropping mercury electrode capillary, or by breaking the anode circuit momentarily. This phenomenon was also shown to be independent of the instrument or electrode system employed and solutions containing other concentrations of aluminium gave similar results. It was noted that this "threshold start potential" effect was most marked with solutions having a pH value of 4 to 4.1. Typical waves obtained on either side of the "threshold" potential are shown in Fig. 2.

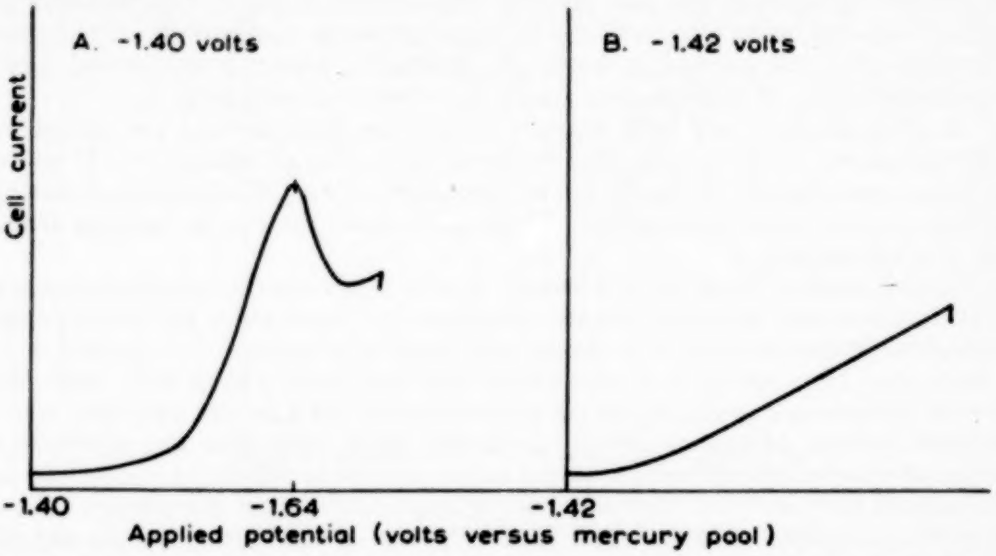

Fig. 2. Aluminium in 0.1*M* calcium chloride. Effect of change in start potential. pH = 4.1.

The effect of pH upon the "threshold" and peak potentials was next investigated. A series of solutions containing 50 μg aluminium in 0.1*M* calcium chloride was prepared as before and the pH values were adjusted by addition of hydrochloric acid or sodium hydroxide before making up to standard volume. After deoxygenation, polarographic determinations were made on each solution using a variety of start potential settings. The pH values of these solutions and their corresponding threshold potentials are listed in Table I.

TABLE I

pH	*Treshold start potential (V vs. mercury pool)*
3.6	—1.45
3.8	—1.44
4.0	—1.43
4.2	—1.39
4.6	—1.36
5.1[a]	—

[a] At this pH value no aluminium wave was obtained at any start potential.

Similar experiments with solutions containing 100 μg aluminium per ml gave results showing the same trend. The threshold potential was, however, in the range of —1.30 to —1.35 V and the change-over was less sharp.

Consideration of these results suggested that the "threshold potential" phenomenon was probably due to large local changes of pH within the diffusion layer around the mercury drop. This would account for the variation of start potential with pH. In single-sweep cathode ray polarography the time between the end of one sweep and the commencement of the reduction wave during the lifetime of the next mercury drop is controlled by the start potential. The value of start potential employed will, therefore, also control the time available for the re-establishment, in the diffusion layer, of the pH conditions existing in the bulk of the solution.

In order to test this theory polarography of the above solutions was repeated on a Cambridge direct writing polarograph. It was found that no threshold potential effect occurred and good waves were obtained for any starting potential that was sufficiently far removed from the foot of the step to allow complete resolution of the wave. This would be expected, in support of the theory, since the rate of application of potential by the cathode ray polarograph is more than 50 times that of the conventional polarograph and unlike conventional polarography, it is applied within the lifetime of only one mercury drop.

Experiments were therefore made to eliminate these local pH changes by buffering the solution.

Polarography in buffered calcium chloride solution

First experiments were made with solutions of aluminium in $0.1M$ calcium chloride buffered with potassium hydrogen phthalate and ammonium acetate at pH 4. The presence of ammonium acetate, however, was found to suppress the aluminium wave completely and subsequent experiments were carried out with potassium hydrogen phthalate alone. A study was next made of the effect of the concentration of this reagent upon the threshold potential.

A series of 10-ml solutions $0.1M$ with respect to calcium chloride and 100 μg/ml with respect to aluminium was prepared. All were adjusted to about pH 4.3 by addition of $0.1N$ sodium hydroxide solution just before making up to final volume. Amounts of $0.05M$ potassium hydrogen phthalate in the range 0.03–0.3 ml were then added. These gave final pH values ranging from 4.1 (0.03 ml added) to 3.9 (0.3 ml added).

The threshold potentials of these solutions were found to move to more negative potentials with increasing buffer concentration and this was accompanied by a decrease in pH. In the presence of 0.03 ml $0.05M$ potassium hydrogen phthalate the threshold value was between —1.50 and —1.52 V and the changeover from one type of wave to the other was no longer sharp and well-defined. Similar experiments with solutions containing other concentrations of aluminium confirmed these results.

The aluminium waves, obtained above, indicated that, although the addition of potassium hydrogen phthalate moved the threshold potential to a more satisfactory value, the accompanying change of pH had an adverse effect on peak shape, especially when the pH fell below 4. A further series was therefore prepared as above, but, after addition of the buffer, the pH was adjusted to 4.0 by addition of sodium hydroxide before making up to final volume.

The results obtained with these solutions showed that for low buffer concentrations (0.03–0.06 ml added) the peak had a rounded top. With higher concentrations (0.15 ml added), however, the peak became sharp and characteristic of a 3-electron reduction. Moreover this shape was not affected by variation of the start potential setting from the smallest applicable value to the threshold potential. Some variation of peak potential with start potential was still observed. The shape of the peaks is shown in Fig. 3.

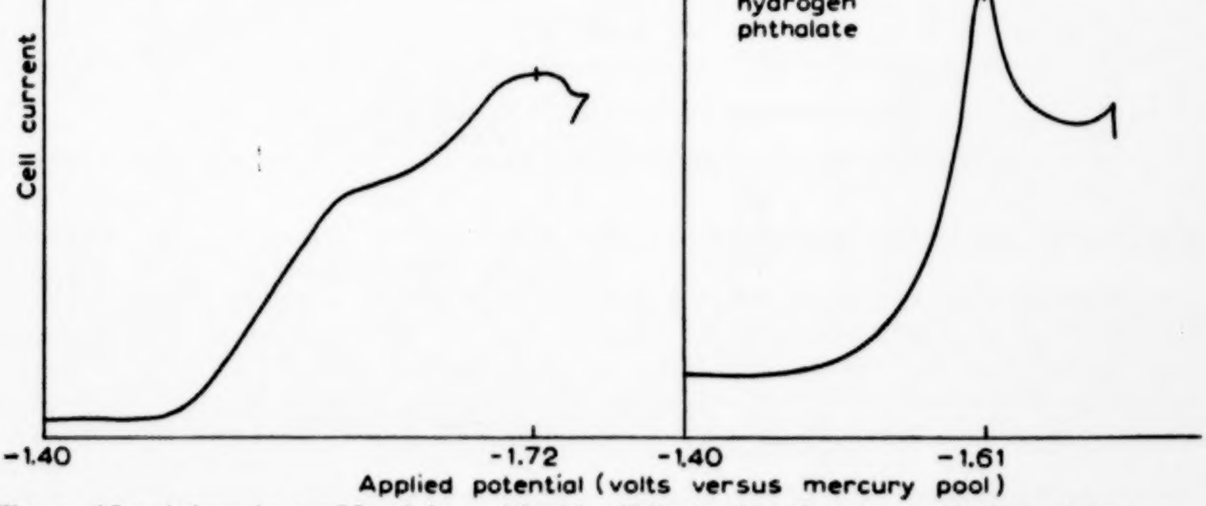

Fig. 3. Aluminium in $0.1M$ calcium chloride. Effect of buffer concentration at pH 4.0.

Higher concentrations of phthalate caused a small wave to appear at the foot of the aluminium peak. This increased in size with increasing buffer concentration (at pH 4) until the shape of the aluminium peak was affected. This is illustrated in Fig. 4.

Polarographic determination of aluminium

The results obtained above were considered to have established the conditions necessary for the satisfactory polarography of aluminium in calcium chloride. A study was therefore made of the relationship between peak height and concentration.

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Three series of solutions were prepared as follows:
5-ml portions of 0.2M calcium chloride solution were placed in beakers and predetermined amounts of standard aluminium solution were added, such that the final concentrations of aluminium were in the ranges 0–100, 0–50 and 0–10 μg/ml. 0.1N sodium hydroxide was added, where necessary to neutralise any acid present and, after addition of 0.15 ml 0.05M potassium hydrogen phthalate to each solution, water was added to bring the volume up to about 9.5 ml. The pH values were then adjusted to 4.0 by addition of hydrochloric acid and the solutions were transferred to 10-ml graduated flasks and made up to volume with washings from the beakers.

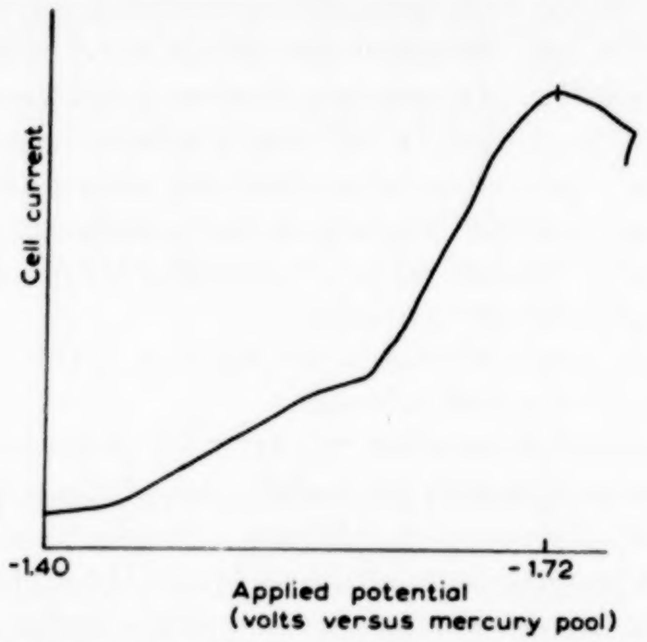

Fig. 4. Aluminium in 0.1M calcium chloride. In presence of $4.25 \cdot 10^{-3} M$ potassium hydrogen phthalate.

An aliquot of each solution was deoxygenated by passage of hydrogen for 10 min and polarographed on the cathode ray polarograph with the start potential control set at —1.45 V. The aluminium peaks obtained varied slightly in the peak potential, but were all sharp and characteristic of a 3-electron reduction. The results obtained are presented in Table II below.

TABLE II

Final aluminium concentration (μg/ml)	*Peak potential (V vs. pool)*	*Peak height**	*Sensitivity setting* (ohms)*	*Peak height per μg/ml*
0	—1.70	7.5	$5 \cdot 10^2$	—
25	—1.71	26.0	$5 \cdot 10^2$	0.74
50	—1.70	47.0	$5 \cdot 10^2$	0.79
75	—1.65	67.0	$5 \cdot 10^2$	0.79
100	—1.66	87.5	$5 \cdot 10^2$	0.795
0	—1.70	7.0	$1 \cdot 10^3$	—
5	—1.78	16.0	$1 \cdot 10^3$	1.8
10	—1.75	26.5	$1 \cdot 10^3$	2.0
25	—1.71	57.5	$1 \cdot 10^3$	2.2
50	—1.72	105.0	$1 \cdot 10^3$	2.0
0	—1.81	12.0	$5 \cdot 10^3$	—
0.5	—1.80	15.0	$5 \cdot 10^3$	6.0
1.0	—1.80	18.0	$5 \cdot 10^3$	6.0
2.0	—1.76	29.0	$5 \cdot 10^3$	8.5
5.0	—1.76	50.0	$5 \cdot 10^3$	7.6
10	—1.73	90.0	$5 \cdot 10^3$	7.8

* Peak heights are given in arbitrary scale divisions on the sensitivity setting on which they were determined. The values of sensitivity setting are given as the value resistance in ohms of the load resistor in the input to the polarograph. The sensitivity is a linear function of the resistance.

DISCUSSION

The cause of the interfering wave appearing at —1.8 V in calcium chloride solutions of concentration higher than 0.3*M* (0.6*M* chloride ion) is not fully understood, but since it appeared only in the presence of aluminium, it may be due to chloro-complex formation, or to replacement of a water sheath by chloride ions. In support of this, previous work has shown that nickel, usually irreversibly reduced, loses its water sheath and moves to its thermodynamically reversible potential in high chloride concentration and that trivalent chromium can exist in several different chloro complexes under similar conditions[7]. A phenomenon, somewhat similar to that attributed here to a change of pH in the vicinity of the drop has been reported in the literature[10]. In this case, however, the element concerned was cobalt and conventional polarography was employed. A similar mechanism was postulated.

The conditions finally established for the satisfactory polarography of aluminium in calcium chloride medium are as follows:

(1) A calcium chloride concentration in the region of 0.1*M*.
(2) A pH value of 4.0 in the final solution.
(3) A final buffer concentration of 0.8 to $1.0 \cdot 10^{-3}M$ potassium hydrogen phthalate.

The results of the experiments on buffer concentration stress the necessity for obtaining a buffer concentration of sufficient capacity to withstand the very large local changes of pH which can occur at the surface of the dropping mercury electrode. The factor of limiting concentration, beyond which the buffer itself begins to interfere with the reaction is also illustrated.

Table II shows that the relationship between peak height and concentration is linear within the wide range of aluminium concentration studied. This linearity may not altogether hold between the ranges, as the results indicate, the strict validity being only within the ranges. Calibration at the level of concentration to be determined is therefore desirable.

In view of the highly negative peak potential of the aluminium wave employed for this determination it was obvious that the method would suffer interference from a large number of common elements. A study of these interferences and means for their elimination was therefore undertaken and will be reported in Part VI of this series[11].

SUMMARY

A study of the polarography of aluminium using the linear-sweep cathode ray polarograph is described. The conditions necessary for obtaining satisfactory aluminium waves in this medium have been established and the relationship between aluminium peak height and concentration examined. The occurrence of unexpected phenomena relating the change of step shape with varying start potential values is described and discussed and a method for overcoming the effects, by buffering, is presented.

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Received January 17th, 1958

SPECTROPHOTOMETRIC DETERMINATION OF IRON IN ZIRCONIUM METAL AND IN ZIRCONYL CHLORIDE*

by

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INTRODUCTION

The use of zirconium as a structural material in building reactors has created a need for analytical methods for determining the impurities present in very pure zirconium. Iron is one of the most common contaminants. Also corrosion studies indicated that higher iron content increased the rate of corrosion in sodium metal.

READ, LAWLER AND DAVIS compiled analytical methods for the determination of impurities in zirconium[1]. Independent analysts listed the 1,10-phenanthroline method for the determination of iron in zirconium, in which the maximum concentration of zirconium tolerated was 1 g/100 ml for a range of 0.05 to 0.25 mg of iron (50 to 250 p.p.m.).

A previous method for the determination of iron in thorium metal[2] in hydrochloric acid medium seemed applicable as a superior technique for the determination of iron in zirconium metal and compounds, and would extend the working range down to 0.02 and up to 0.5 mg of iron. Further, while the iron may be determined without preliminary separation of the zirconium in samples containing a maximum of 1.0 g of the hydrated zirconyl chloride (0.28 g zirconium) in a final volume of 25 ml, an additional procedure, that for removing 80% of the zirconium per separation by the hydrochloric acid precipitation method[3] would enable the iron content to be concentrated 5 to 10-fold and lower the detection limit of iron in zirconium to 0.004 mg (4 p.p.m.).

Reagents

Standard iron solution. Dissolve 0.10 g iron wire in 10 ml of concentrated hydrochloric acid. Add 1 to 2 drops of 30% hydrogen peroxide. Add 10 ml of water; boil to decompose hydrogen peroxide. Dilute to 1 l with a stock solution of 1:1 hydrochloric acid. One ml equals 0.1 mg of iron.

Hydrochloric acid solution (1:1). Prepare 20 l (5 gal.) of 1:1 hydrochloric acid for use in all samples and standards.

Iron-free zirconyl chloride. Reagent grade $ZrOCl_2.8H_2O$ was re-crystallized as directed in the procedure to remove iron, and a spectrophotometric curve (Fig. 1) of the residue was obtained. As a confirmatory test, the residue was recrystallized and no iron was found in the filtrate.

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* This article is based on studies performed for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

PROCEDURE

Determination of iron in zirconium metal

Direct method (Fe > 20 p.p.m.)

Transfer 1.00 g of zirconium metal to a platinum dish and cover the sample with 3 ml of water. Add 2.5 ml of hydrofluoric acid, dropwise, until the metal completely dissolves. Add 4 ml of concentrated hydrochloric acid and 1.2 g of solid boric acid. Evaporate to near dryness in the dish. Add about 75 ml of 1:1 hydrochloric acid. Heat until the entire sample is in solution. Then transfer the solution to a 150-ml beaker with 1:1 hydrochloric acid. Add 1 to 2 drops of 30 per cent hydrogen peroxide and evaporate to half-volume. Transfer to a 100-ml volumetric flask and dilute to volume with the prepared 1:1 hydrochloric acid. Measure the intensity at 360 millimicrons on a Beckman spectrophotometer, Model D. U. For the blank, use an iron-free $ZrOCl_2$ sample solution which has been treated in the same manner as the samples. Calculate the iron content from the standard curve, noting that the iron content on the curve is for a 25-ml volume.

Pre-concentration method (Fe < 20 p.p.m.)

Transfer 5.00 g of zirconium metal to a large platinum dish. Cover the metal with 5 ml of water and add 13 ml of hydrofluoric acid, dropwise, until all the zirconium metal has dissolved. Add 20 ml of concentrated hydrochloric acid and 6 g of solid boric acid. Evaporate to near dryness over an asbestos gauze. Add 10 ml of 3:1 hydrochloric acid. Cool and filter. Wash with a minimum amount of cold 3:1 hydrochloric acid. Transfer the filtrate to a 150-ml beaker with water. Dilute to about 75 ml with 1:1 hydrochloric acid and proceed as for 1 g zirconium metal by adding hydrogen peroxide, evaporating to small volume, then taking up in the 1:1 hydrochloric acid solution and diluting to volume.

If greater sensitivity is needed, increase the sample size to 10 g of zirconium and add double the amount of reagents required for a 5-g sample.

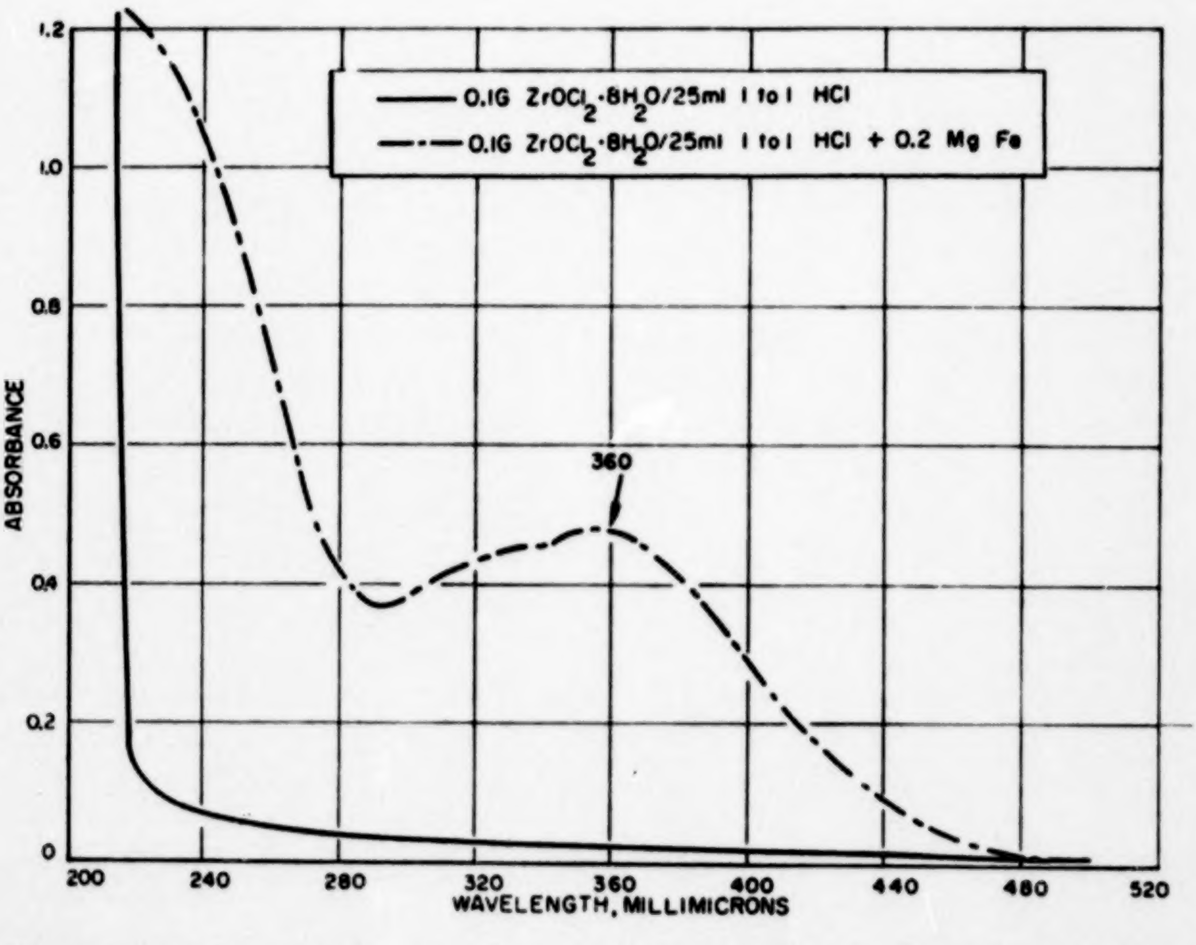

Fig. 1. Spectrophotometric curves of hydrated zirconyl chloride with and without iron.

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Determination of iron in hydrated zirconyl chloride

Direct method (Fe $>$ 20 p.p.m.)

Weigh 1.00 g of hydrated zirconyl chloride (1 g $ZrOCl_2.8H_2O$, 0.28 g Zr) into a 100-ml beaker. Dissolve with 1 to 2 ml of water. Add 25 ml of 1 : 1 hydrochloric acid and 2 drops of 30% hydrogen peroxide. Boil to half-volume. Transfer the solution to a 25-ml volumetric flask with the specially prepared 1 : 1 hydrochloric acid solution and dilute to volume. Measure the intensity at 360 mμ on a Beckman spectrophotometer, Model D. U. For the blank, use a solution which has been treated in the same manner as the sample. Calculate the per cent iron from the standard curve (25-ml volume).

Pre-concentration method (Fe $<$ 20 p.p.m.)

Transfer 25 g of the hydrated zirconyl chloride to a 100-ml beaker. Dissolve with 25 of ml water. Add 35 ml of concentrated hydrochloric acid and evaporate to near dryness. Add 15 ml of 3 to 1 hydrochloric acid. Cool and filter. Wash with a minimum amount of cold 3 to 1 hydrochloric acid. Transfer the filtrate to a 150-ml beaker with water, add peroxide, evaporate to half-volume and proceed as described as under the direct method for hydrated zirconyl chloride except that the final volume will be 100 ml.

Preparation of the standard curve

To a series of six 50-ml beakers add 1 g each of iron-free hydrated zirconyl chloride (0.28 g Zr) (prepared from c.p. $ZrOCl_2.8H_2O$ by the precipitation process described above) and add 0, 0.1, 0.2, 0.3, 0.4, and 0.5 mg of standard iron solution, respectively to each. Add one drop of 30% hydrogen peroxide and 25 ml of 1 : 1 hydrochloric acid and evaporate to half volume. Transfer the warm solutions to 25-ml volumetric flasks and dilute to volume with the specially prepared 1 : 1 hydrochloric acid solution. Mix and cool. Adjust to volume and mix again.

Measure the intensities at 360 mμ on a Beckman D.U. spectrophotometer and plot the standard curve.

RESULTS

Samples of hydrated zirconyl chloride weighing 20 to 25 g were selected for analysis. The bulk of the zirconium was removed by the hydrochloric-acid precipitation method[3] and the final filtrate was analyzed for iron (Table I). The hydrated zirconyl chloride samples, calculated as zirconium metal, were found to contain 0.003% iron.

Samples of zirconium metal from many sources were analyzed for iron in sample-sizes ranging from 0.5 to 1.0 g zirconium metal without prior separation of the zirconium. They varied in iron content from 0.02 to 0.07% (Table II). No purer samples were available.

TABLE I

Fe IN $ZrOCl_2.8H_2O$

HCl-SEPARATION OF BULK OF ZIRCONIUM

No.	*Weight* (*g*)	*Volume* (*ml*)	*Absorbance* 360 *mμ*	*Fe* *mg*	*Fe* %
1	20.0 (5.7 g Zr)	50	0.166	0.148	0.003
	20.0 (5.7 g Zr)	50	0.186	0.164	0.003
2	25.0 (7.1 g Zr)	25	0.511	0.230	0.003
	25.0 (7.1 g Zr)	25	0.476	0.214	0.003
3	20.0 (5.7 g Zr)	25	0.425	0.194	0.003
	20.0 (5.7 g Zr)	25	0.411	0.188	0.003

TABLE II

Fe IN Zr METAL

Direct method

No.	*Description*	*Weight (g)*	*Volume (ml)*	*Absorbance 360 mμ*	*Fe* mg	*Fe* %
1	Crystal bar	1.0001	100	0.414	0.728	0.073
1	Crystal bar	1.0000	100	0.388	0.667	0.067
2	Leached C.B.	1.0001	100	0.172	0.272	0.027
2	Leached C.B.	1.0002	100	0.166	0.260	0.026
3	"N" polished	0.8171	100	0.145	0.260	0.032
3	"N" polished	0.4021	50	0.147	0.130	0.032
4	"B 9" Series	1.5849	100	0.359	0.688	0.043
4	"B 9" Series	0.5508	50	0.254	0.244	0.044
5	"B 8" Series	1.3730	100	0.345	0.660	0.048
5	"B 8" Series	0.5259	50	0.243	0.230	0.044
6	"B 1" Series	1.4666	100	0.358	0.688	0.047
6	"B 1" Series	0.4649	50	0.239	0.220	0.047
7	"C 13" Series	1.5400	100	0.375	0.720	0.047
7	"C 13" Series	0.4575	50	0.234	0.220	0.048

Efficiency of purification

Since no pure (iron-free) sample of zirconium metal was available, a simulated sample of zirconium was used. Two 25-g samples of $ZrOCl_2.8H_2O$, containing 90 p.p.m. Fe were purified according to the procedure. The equivalent of 90 p.p.m. of iron was recovered in the filtrate (Table III). The absorbance of the purified residual solution was equal to that of the reference solution, which indicated the absence of iron (Fig. 1). In order to recheck this result, the precipitate was reworked, and no iron was recovered in the filtrate.

TABLE III

SIMULATED ANALYTICAL RECOVERIES OF IRON FROM ZIRCONIUM METAL

	Starting material (g)		*Iron content (p.p.m.)*			*Further reworking of residue for Fe*
	Zr	*$ZrOCl_2.8H_2O$*	*Initial*	*Recovery in analysis*	*Found in residue*	
(1)	7.1	25.0	90	90	none detected[a]	none detected[a]
(2)	7.1	25.0	90	90	none detected[a]	none detected[a]

[a] Minimum detectable is 3 p.p.m. in 7.1 g Zr

DISCUSSION

Spectrophotometric curves (Fig. 1) of 1:1 hydrochloric acid solutions containing zirconyl chloride with and without iron suggested that iron could be determined in zirconium by the hydrochloric-acid method. When iron was present, maximum ab-

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sorbance was observed from 340 to 360 mμ. When 0.0 to 0.5 mg portions of iron were added to 1-g solutions of zirconyl chloride, straight-line absorbance plots were obtained at all of these wavelengths. Varying the concentration of zirconyl chloride from 0 to 1.0 g per 25 ml of 1:1 hydrochloric acid in synthetic samples containing 0 to 0.5 mg of iron produced curves which followed Beer's Law at 360 mμ.

Standards were run with and without boric acid. Concentrations of 0.5 and 1.0 g solid boric acid did not cause any interference in absorbance readings of iron standards containing 1.0 g $ZrOCl_2.8H_2O$. Standard curves prepared in the same manner as the sample showed that the addition of both hydrofluoric and boric acid did not introduce interferences.

In order to reduce the possibility of any interference from any iron which may be present in the reagents used, a reagent blank and standard curve are prepared in the same manner as the sample. Blanks were also prepared by purifying $ZrOCl_2.8H_2O$ by the recrystallization process. Zirconyl chloride itself in 1:1 hydrochloric acid solution shows a slight absorbance at 360 mμ.

Copper and tin[4], if present in the zirconium metal will interfere in the method described here, and should be removed.

SUMMARY

Iron, present in zirconium metal or in zirconyl chloride, may be determined spectrophotometrically in 1:1 hydrochloric acid solution without prior separation from the zirconium. In a 1:1 hydrochloric acid solution, at the solubility limit of zirconyl chloride (0.28 g zirconium per 25 ml), 20 p.p.m. of iron may be detected.

When smaller amounts of iron are to be determined (4 p.p.m.), a larger starting sample (5 g) of zirconium is crystallized from a 3:1 hydrochloric acid solution which reduces the lower limit of detection of iron to 4 p.p.m.

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Received December 17th, 1957

SPECTROPHOTOMETRIC CONSTANTS IN GLACIAL ACETIC ACID OF 2,2′-DIPYRIDINE AND ITS 4,4′-DISUBSTITUTED DERIVATIVES AS Fe(II) COMPLEX CATIONS

by

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INTRODUCTION

The spectrophotometric constants of some of the ferrous-1,10-phenanthrolines as their Fe(II) complexes in aqueous solution are appreciably modified through the influence of other solvents[1].

The ferroine phenanthrolinium tris complex ion has been studied in glacial acetic acid as solvent by BRANDT AND HOWSMON[2].

The present report involves the study of 2,2′-dipyridine and eleven 4,4′-disubstituted derivatives as their Fe(II) complex cations in glacial acetic acid. A similar study[3] has been made of the same chelation complexes in aqueous solution. Comparison of physical constants (wave length of maximum absorption and molar absorptivity) is made. 4,4′-diphenyl-2,2′-dipyridine has been added and 4,4′-dinitro-2,2′-dipyridine dropped from the reagents previously[3] studied.

ORGANIC LIGANDS STUDIED

Besides 2,2′-dipyridine, the 4,4′-disubstituted -2,2′-dipyridines following group substitutions in both positions were included:

Unsubst'd,	CH_3,	C_2H_5,	Br,	Cl,	OCH_3,	OC_2H_5,	OC_6H_5,	$COOC_2H_5$,	$CONH_2$,	COOH and	C_6H_5
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII

PREPARATION OF REAGENTS

Glacial acetic acid solutions of Fe(II) are subject to pronounced air oxidation. Ferric solutions were used as controls with hydroquinone (soluble in HOAc) as the most suitable reductant. Spectrophotometric absorption in the 500–600 mμ region by its oxidation product, quinone, is insignificant. Accordingly, pronounced absorption by quinone over the 340–450 mμ range made calculations impractical of molar absorptivities therein.

Preparation of ligand solutions

Weighed samples of all ligands were dissolved in glacial acetic acid to give 0.01 formal solutions. Ligands X and XI were not sufficiently soluble and were employed as their saturated solutions.

Sodium acetate solution

0.01 formal in glacial acetic acid.

Hydroquinone

1.0 g of reagent dissolved in 100 ml of glacial acetic acid.

1,10-Phenanthroline

0.01 formal solution of the ligand monohydrate in demineralized water.

Standard iron solution

0.363 g of ferrous perchlorate hexahydrate dissolved in 500 ml of glacial acetic acid. Standardization as the 1,1-phenanthroline Fe(II) complex indicated 0.00192 millimoles of iron per g of solution.

Glacial acetic acid

Reagent grade, no additional purification.

Qualitative test for chelation

To 5-ml portions of glacial acetic acid, there were added 1 ml each of solutions of ligand, sodium acetate, hydroquinone, and standard iron. The solutions in glass-stoppered test tubes were thoroughly mixed. Complex formation, noted by color, and observed as to stability for 24 h, was established for ligands I to XII inclusive (4,4′-diamino-2,2′-dipyridine gave only feeble color reaction and was not further tested).

Determination of spectrophotometric constants

For this purpose a Cary Recording Spectrophotometer, model 14 M, was employed using 10-mm silica cuvettes.

Solutions for determination of their absorption were prepared as follows:

To 25-ml, glass-stoppered volumetric flasks containing weighed samples of the standard iron solutions, there were added, 1-ml portions of hydroquinone and sodium acetate, and 2-ml portions of ligand solution. The contents of the flasks were diluted to the mark with glacial acetic acid, mixed, and immediately subjected to spectrophotometric examination. (Excess ligand, undissolved in the case of reagents IX and X were filtered out before optical examination.)

Triplicate individually complexed ligand solutions of increased amounts of iron thus examined gave data for the calculation of molar absorptivity. Beer's Law was found to be valid over the range 1 to 4 mg of iron. All solutions were stored 60 days without appreciable alteration. The data are recorded in Table I.

From the data of Table I it is observed that altered wave lengths of maximum absorption equal to or greater than 3 mμ are produced in glacial acetic acid as

TABLE I

SPECTROPHOTOMETRIC DATA FOR THE IRON(II) COMPLEXES OF LIGANDS I TO XII IN GLACIAL ACETIC ACID

Ligand	*Wave length of max. absorption in mμ* *1*	 *2*	*Average molar absorptivity maximum for 2*
I	350 (349)	520 (522)	8930 (8710)[a]
II	354 (354)	527 (528)	9620 (9340)[a]
III	355 (355)	528 (529)	10090 (9880)[a]
IV	356 (357)	535 (534)	8910 (5550)[a]
V	356 (355)	534 (532)	8250 (8300)[a]
VI	360 (357)	538 (525)	7340 (6680)[a]
VII	361 (359)	538 (525)	7580 (7660)[a]
VIII	360 (363)	541 (540)	8310 (8060)[a]
IX	392 (384)	544 (541)	16440 (14150)[a]
X	388 (384)	543 (540)	16110 (14940)[a]
XI	387 (378)	543 (540)	8210 (14760)[a]
XII	382 (386)	547 (552)	20800 (21280)[b]

Values in parentheses taken (a) from SMITH AND BANICK[3], (b) from previous results[4]. Both these cases refer to buffered aqueous solutions.

compared to aqueous solutions, only in the case of ligands VI, VII, IX, X, XI and XII. No significant change in magnitude of molar absorptivity was found save in the case of ligands IV and XI.

In the case of ligand IV this increase of approximately 44% is possibly due to the absence of hydrolytic effects in the displacements of bromine in glacial acetic acid. A decrease in value in the case of ligand IX is probably due to the lowered solubility of the chelation reagent as compared with the higher value in aqueous solution.

Spectrophotometric absorption curves

Plots of the spectrophotometric absorption curves obtained in these studies in glacial acetic acid did not differ materially in general contour from those obtained for the same complexes in the previous studies[3,4] in water as solvent. This fact indicates that wave lengths relation to absorption effects, are minor in influence as compared to structural alterations in the ligand, brought about in the use of notably different solvents.

ACKNOWLEDGEMENT

The study of the ligands employed in this work was made possible through their synthesis, details of which will be published elsewhere, by Professor FRANCIS CASE and GERHARD MAERKER of Temple University, Philadelphia. Appreciation is herein expressed for this cooperation.

SUMMARY

A continuing study of previous work involving the same organic reagents — 2,2′-dipyridine and its 4,4′-disubstituted derivatives as Fe(II) complex cations — in glacial acetic acid and in buffered aqueous solutions. Determination of the spectrophotometric constants (wave length of maximum absorption and molar absorptivity) in glacial acetic acid for the visual and near ultraviolet region of the spectrum has been supplied.

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Received December 18th, 1957

BUCHBESPRECHUNGEN

Hochfrequenztitration, die chemische Analyse mit Hochfrequenz ohne galvanischen Kontakt zwischen Lösung und Elektrode, von KURT CRUSE UND REINHARD HUBER, Verlag Chemie, Weinheim/Bergstr., 1957, xii + 198 Seiten, 152 Abb. im Text, Kart. DM 22.—.

Das Buch, das in der Reihe kleiner Monographien der Zeitschriften *Angewandte Chemie* und *Chemie-Ingenieur-Technik* erschienen ist, ist nach einer Reihe von Referaten in verschiedenen Zeitschriften und nach einem Kapitel REILLY's im Buche *New Instrumental Methods in Electrochemistry* von DELAHAY, die erste Monographie, die sich mit diesem jüngsten Zweig der Elektrochemie beschäftigt. Die Hochfrequenzmethoden unterscheiden sich von den anderen Methoden der Elektrochemie besonders dadurch, dass das studierte chemische System sich nur im Kraftfeld befindet und nicht im Kontakt mit der Elektrode, sodass während der Messung keine Elektrodenreaktionen, also chemische Reaktionen durchlaufen. Die Hochfrequenzmethoden sind also mehr physikalische als physiko-chemische Methoden. Die Konstruktion der Geräte für solche Messungen stellt an den Chemiker grosse Anforderungen, was die Kenntnisse der Elektronik betrifft. Daher ist es von Vorteil, dass ein Physikochemiker, Prof. CRUSE, und ein Physiker, Dr. HUBER, gemeinsam das Buch verfassten.

Die Monographie ist in drei Hauptkapitel geteilt, von denen das erste die Theorie der Hochfrequenzmessungen eingehend behandelt, das zweite der Bedeutung dieser Theorie für praktische Verwendung in der chemischen Analyse, und das dritte der Mess- und Gerätetechnik gewidmet ist.

Die Verfasser entwickeln die Theorie von den Grundbegriffen der Wechselstromphysik (komplexe Natur des Wechselstromwiderstandes, der Anteil der Blindkomponente) und von der klassischen Kohlrausch-Zelle für Leitfähigkeitsmessungen leiten sie die Eigenschaften der Kapazitäts- oder Induktionszelle für Hochfrequenzmessungen ab. Auf den Ersatzschaltbildern dieser Zellen berechnen sie die Abhängigkeiten der elementaren Messgrössen, wobei die Aufmerksamkeit in der ersten Stelle der Empfindlichkeit und Eindeutigkeit der Messung gewidmet ist. Es folgt ein Absatz über die Funktion dieser Zellen im Schwingkreis, welches mit einer Übersicht des Durchschnitts der Empfindlichkeit und der Messgrössen bei den Grundtypen der Zellen für Wirkkomponente- und Blindkomponentemethode schliesst. Unter den Abweichungen vom einfachen Ersatzbild ist als Kuriosität der Topfresonator angeführt, der für diese Zwecke bis jetzt nur einmal verwendet wurde. Endlich ist hier auch die, von denselben Autoren ausgearbeitete, sogenannte RC-Titration erwähnt. Zum Schluss dieses ersten Teiles ist die Theorie der verwendeten Röhren-Oszillatoren (Meissner, Hartley, Colpitt, Clapp, Huth-Kühn, Heegner, Franklin) und der Messmethoden gegeben. Es ist Schade, dass die, eine Übersicht der Methoden der Hochfrequenztitrationen zeigende Schlusstafel dieses Kapitels nicht mit einer schematischen Darstellung der Oszillator Schaltbildern, wie es die Verfasser bereits in ihren Referaten veröffentlichten, ergänzt wurde.

In der Einleitung zum zweiten Teil, welche die praktische Anwendung der Theorie umfasst, machen die Autoren in einem Satz — welcher das Motto des Buches sein könnte — darauf aufmerksam, wie wichtig die Geschicklichkeit des Experimentators ist, der die Leitfähigkeit und die dielektrische Eigenschaften des Messystems beurteilen muss, um die Versuchsbedingungen für optimale Messungen zu wählen. Nach kurzer Behandlung des Einflusses der Frequenz, der dielektrischen Konstante, der Leitfähigkeit, der Temperatur und der Qualität des Lösungsmittels führen die Verfasser mögliche Titrationskurven an und geben eine Übersicht der bisherigen Anwendung dieser Titrationstechnik für einzelne chemische Systeme. Zum Schluss ist die Untersuchung von Papierchromatogrammen mittels Hochfrequenz erwähnt.

Das dritte Kapitel ist der Mess- und Gerätetechnik der Hochfrequenztitrationen gewidmet. Es sind hier die Konstruktionen der Messzellen, einschliesslich der Konstruktion des Topfresonators von BLAEDEL und MALMSTADT angeführt. Es folgen die Messmethoden (die Messungen von Strom und Spannung und etwas ausführlicher die Messungen der Frequenz), und dann kurz die Stromversorgung für die Titrimeter. Am Ende sind einige Schaltbilder wichtiger Typen von Hochfrequenztitrimeter angeführt.

Das Buch ist mit einer Tafel von, in den Schaltbildern verwendeten Symbolen, mit einem kurzen Verzeichniss englischer Fachausdrücke, mit gutem Register und mit einem, bis auf einige Ausnahmen vollständigen Verzeichnis der Literatur versehen.

Die Autoren haben berechtigterweise den Schwerpunkt dieser Monographie in den theoretischen Teil versetzt (das zweite Kapitel kann diese Absicht nur unterstreichen) und der Leser, der vielleicht praktische Anweisung suchend, den ersten Teil überspringt, wird zu den ersten Kapitel immer wieder zurückkehren müssen. Diese Tatsache geht schon aus der Grundforderung dieser Methode hervor, welche nicht nur einen guten Experimentator, sondern auch einen Chemiker-Elektroniker beansprucht. Die vorliegende Monographie gibt eine so gründliche Einleitung in dieses junge, und noch selten an Hochschulen vorgetragene Gebiet, dass der Leser die Vorteile der Methode mit gutem Erfolg ausnützen kann. In Hinsicht auf den Umfang dieser kleinen Monographie ist es auch begreifbar, dass die eigentliche analytische Verwendung nur auf einige Seiten beschränkt wurde.

Das Buch ist gut und klar geschrieben, mit zahlreichen Formeln, Graphen und Bildern illustriert, und sorgfältig gedruckt (dem Rezensenten gelang es nur einen Druckfehler zu finden). Sein Preis scheint jedoch ziemlich hoch zu liegen.

Dieses Buch wird, mit der vorbereiteten Monographie von F. OEHME über DK-Messungen, die in derselben Reihe des Verlags Chemie erscheinen soll, bestimmt einen guten Grund der Literatur dieses jungen Zweiges der physikalischen Chemie und der chemischen Analyse bilden.

L. JENŠOVSKÝ (Prag)

Handbuch der analytischen Chemie, herausgegeben von W. FRESENIUS UND G. JANDER, Springer Verlag, Berlin, 1957.

Elemente der fünften Hauptgruppe, Band Va (*a*) xxiv + 244 Seiten, DM 54.—.
Stickstoff, Quantitative Bestimmungs- und Trennungsmethoden, bearbeitet von W. LEITHE, Oesterreichische Stickstoffwerke, Linz.

Das vorliegende Werk behandelt in ausführlicher und doch übersichtlicher Weise die bekannten Bestimmungsmethoden des Stickstoffes in seinen verscheidenen Vorkommen. In einem ersten Kapitel sind nacheinander die Bestimmungen des elementaren Stickstoffes der Stickstoff-Metallverbindungen, und des organisch gebundenen Stickstoffes besprochen. Naturgemäss nimmt darin der letzte Abschnitt den weitaus grössten Raum ein. Besondere Beachtung haben die Mikroanalysen des Stickstoffes gefunden (Mikro-Kjeldahl, Elementaranalyse nach PREGL, etc.). Das zweite Kapitel des Buches behandelt die Analyse des Stickstoffes in seinen anorganischen Verbindungen. (§§ 4-11, Natriumamid, Hydrazin, Stickstoffwasserstoffsäure, Stickoxyde, Hydroxylamid, untersalpetrige Säure, salpetrige Säure, Salpetersäure).

Auch hier sind die Verfahren der modernen Analyse mit einer besonderen Sorgfalt behandelt. (Konduktometrie, Polarographie.) Nach unserer Erfahrung zeigt das Buch den enormen Vorteil, dass neben den rein rezeptmässigen Angaben der Analysen auch deren Theorie und die möglichen Fehlerquellen einer einwandfreien Bestimmung besprochen werden.

Elemente der fünften Nebengruppe, Band Vb, 520 Seiten, DM 118.—.
Vanadin, Niob, Tantal – Quantitative Bestimmungs- und Trennungsmethoden des Vanadins, Niobs und Tantals, bearbeitet von Dr. G. J. VAN KOLMESCHATE, Direktor des analytischen Institutes-TNO, Delft.

Das Buch behandelt zuerst auf 300 Seiten die Analyse des Vanadins. Nach einer kurzen Einführung allgemeiner Natur folgen die gravimetrischen, volumetrischen, polarographischen, kolorimetrischen, spektrographischen Bestimmungsmethoden. Für jede Bestimmungsart sind die Vor- und Nachteile ihrer Anwendung in den verschiedenen Fällen besprochen und darüber hinaus die genauen Rezepte für die wichtigsten Fälle gegeben. In einem separaten Abschnitt sind noch die zum Teil subtilen Trennungsmethoden des Vanadins behandelt.

Die Analytik der beiden Metalle Niob und Tantal, deren technische Bedeutung in letzter Zeit bedeutend zunimmt, findet auf 220 weiteren Seiten des Buches Platz. Die Gliederung des Materials ist insofern ein wenig kompliziert geworden, weil sich Niob und Tantal doch nicht überall auf den gleichen Nenner bringen lassen. Die verwendete Dezimalklassifizierung vermag jedoch auch hier weitgehend Ordnung zu schaffen, sodass sich der Leser trotzdem rasch zurecht findet.

H. KELLER (Genf)

THE TITRIMETRIC DETERMINATION OF CARBON DIOXIDE WITH SPECIAL REFERENCE TO THE DETERMINATION OF CARBON IN ORGANIC COMPOUNDS

by

R. BELCHER, J. H. THOMPSON AND T. S. WEST

Department of Chemistry, The University, Birmingham (Great Britain)

INTRODUCTION

The method for determination of carbon dioxide by absorption in alkaline solution, followed by back-titration of the excess of alkali is well-known and widely used. The conventional absorbents are sodium hydroxide and baryta, but the latter is generally preferred because barium carbonate is sparingly soluble and does not readily redissolve at the end-point when an indicator which changes in the pH range 8 - 11 is used. The necessity for carrying out two titrations when sodium hydroxide is the absorbent may be avoided if the carbonate is precipitated by the addition of barium chloride. This technique was used by JOHANSSON[1], but he collected the precipitated barium carbonate which was then converted to the iodate and determined iodometrically. In most methods excess of barium chloride is present, even when baryta is used, in order to depress the solubility of the carbonate by the common ion effect.

Organic solvents were used to increase the solubility of carbon dioxide by VAN NIEUWENBURG AND HEGGE[2]; they used a mixture of freshly distilled aniline, ethyl alcohol and baryta as absorbent. More recently BLOM AND EDELHAUSEN[3] have examined other solvents; they finally recommended either pyridine or acetone as absorbent and they determined the carbon dioxide by continuous titration with sodium methoxide using thymol blue as indicator. An aqueous baryta/barium chloride absorbent was preferred, however, during the present investigation.

SÖRENSEN AND ANDERSEN[4] noted that when a solution containing a soluble carbonate and hydroxide was treated with excess of barium chloride and titrated with hydrochloric acid to a phenolphthalein end-point, high recoveries of carbonate and low recoveries of hydroxide were obtained. This they attributed to the precipitation of a basic barium carbonate. LINDNER[5] showed that the barium carbonate so precipitated was contaminated with silicate from the glass vessels, and that baryta stored in glass vessels for several months was unfit for use as an absorbent[6]. This represents another possible cause of high carbonate values, but the error is probably not as important as LINDNER first believed, for later[7] he still obtained high results even though silica-free solutions were used. LINDNER also noted that temperature was an important factor; the precipitation should be carried out in the cold, in order to obtain a granular deposit with less occluded impurity, and to avoid increased solubility of the carbonate at higher temperatures. POETHKE AND MANICKE[8] confirmed these findings.

LINDNER AND FIGALA[9] found that errors are caused by the occlusion of hydroxyl ions by precipitated barium carbonate. They recommended heating the solution for 10 min after a preliminary end-point had been obtained, and then continued the titration. Subsequently, LINDNER[10] demonstrated that the absorption of carbon dioxide by baryta was sometimes incomplete especially when high concentrations of carbon dioxide were encountered, (*e.g.* in the rapid combustion of a highly carbonaceous compound). A general description of some of the factors involved in the absorption of carbon dioxide by barium hydroxide has been given by LINDNER[10].

EXAMINATION OF THE METHOD

The errors which must be considered can be classified conveniently, as given below, under three headings. A fourth source of error (contamination by atmospheric carbon dioxide) may occur in the transference of the barium hydroxide solution before and after the combustion. However, precautions to avoid this error would have required complicated apparatus and it was thought sufficient to tandardise the procedures rigidly.

Errors involved in the absorption of the carbon dioxide

The efficiency of barium hydroxide as an absorbent for carbon dioxide is dependent on surface effects, hence the design of the absorbing vessel is perhaps the most important single factor involved in the determination. In a dynamic system, such as the one described below, the speed of absorption depends on the rate of diffusion of the carbon dioxide towards and through the periphery of the gas-bubble, so that the formation of the film or barrier layer of barium carbonate naturally reduces the efficiency of the absorption.

From the preliminary discussion it can be seen that the efficiency of the absorption may be increased by various factors.

Increasing the temperature of the absorbing solution would certainly speed the diffusion of the carbon dioxide, reduce the surface tension, and thus aid the absorption, but these effects would be offset by the tendency for the precipitate formed from hot solution to occlude basic constituents[7]. The *use of a strong barium hydroxide solution* is not to be recommended, for the strength of the absorbent and of the titrant should be approximately equal so that the back-titre is significantly different from the blank and so that the titres are not excessive. An approximately 0.05*N* baryta solution was used in this investigation. Absorption could be made more efficient by the use of a *slower gas flow* or by placing a *distributor bulb* in the assembly to dilute the carbon dioxide. However, at low flow rates, gas dilution is not necessary and at high flow rates the carbon dioxide is automatically diluted.

Several *designs of absorber* were examined. The Grote type absorber (Fig. 1) was eventually selected because partial absorption occurs before the gas passes through the sinter and complete absorption is obtained from the small bubbles in the upper chamber. The use of more than one absorber was not found to be necessary.

Surface tension can be reduced by adding a substance such as ethanol to the absorbent but this addition did not seem to have any significant effect. *The solubility of the barium carbonate* was reduced (common ion effect) by the addition of barium chloride (20% w/v) to the absorbent; a 20% barium chloride solution was used as the wash liquid.

At this stage in the investigation the mean deviation was ± 0.5% carbon, and the titration values, from the blank runs, as well as the carbon percentages were slightly variable. (Blank titres were within *ca.* ± 0.1 ml 0.05N acid).

Errors involved in the back-titration of the excess baryta

Surface interactions, e.g. adsorption of hydroxide, may cause trouble here but these are more conveniently dealt with in the next section. To avoid errors from the *attack of the acid* on the precipitated barium carbonate, the solution was stirred magnetically throughout each titration and the acid was added dropwise. The visual method of *end-point detection* caused difficulty owing to the opalescence of the precipitate. Thymol blue/cresol red, phenolphthalein and *o*-cresolphthalein were tested and the last named was preferred.

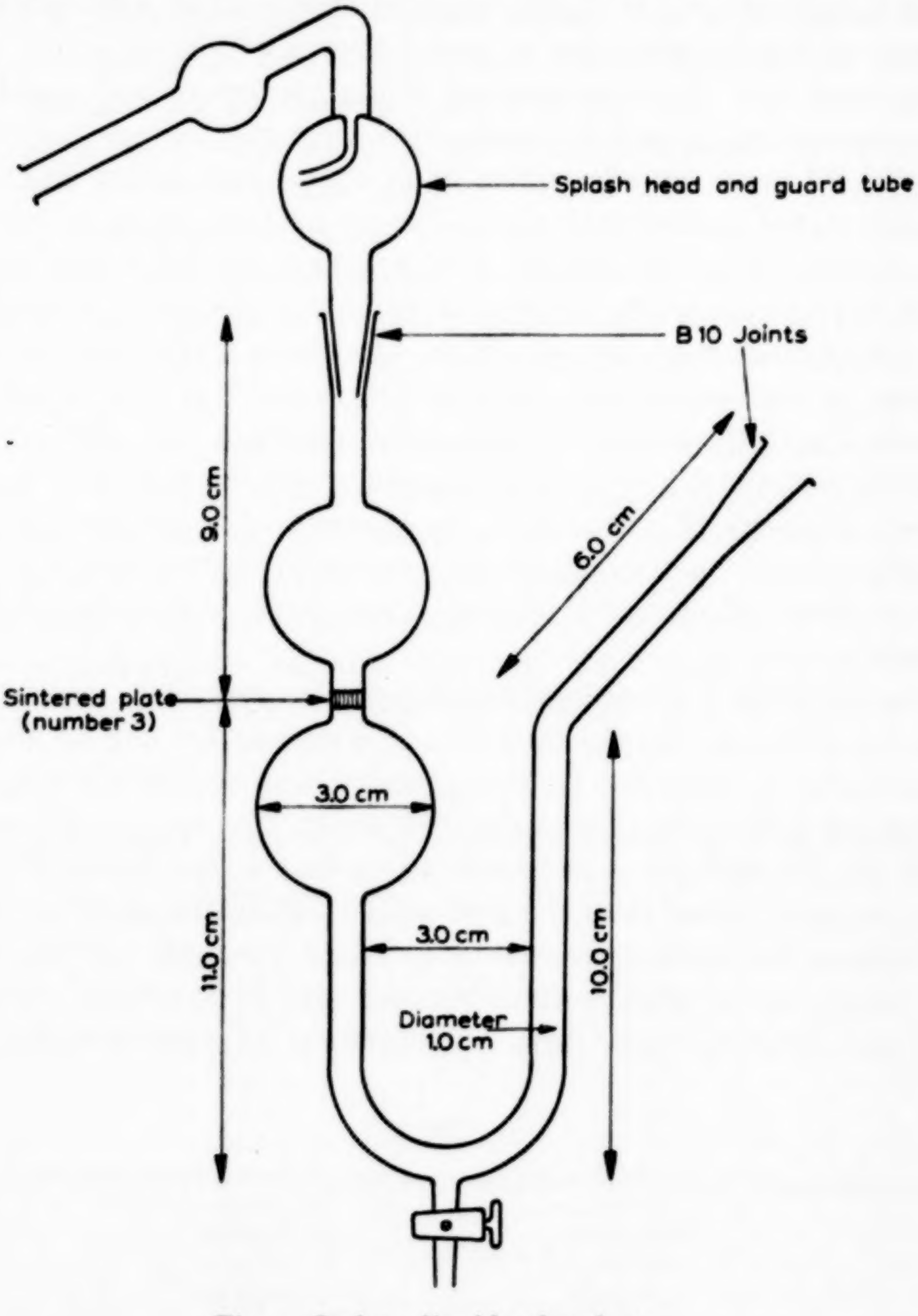

Fig. 1. Carbon dioxide absorber.

The absorption of atmospheric carbon dioxide is an obvious source of error, hence the technique of filling and washing the absorber was kept to a standard routine.

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Since the dropwise titration took some time, it was done under a stream of carbon dioxide-free nitrogen. Complete elimination of any possibility of carbon dioxide uptake would have required complex apparatus and the standardisation of technique was considered sufficient.

A detailed account of the experiments which confirmed the above conclusions is omitted in this paper.

Errors caused by surface interaction

A possible source of error is the interaction of the alkali with silicic acid derived from the glass of the absorber, the conical flasks, the burette or the storage vessel. It was considered that the standardised filling procedure and regular blank runs would overcome errors caused by interaction with the storage bottle and burette. Other errors could occur by adsorption of hydroxyl ions either on the glass vessels or on the precipitated barium carbonate. The precipitation of basic borium carbonate, which was mentioned by SÖRENSEN AND ANDERSEN[4], has never been completely proved, and results previously attributed to this compound are probably best explained by adsorption or occlusion effects. Occlusion could only take place during the formation of the precipitate, and would be difficult to remedy. Previously, LINDNER AND FIGALA[9] considered that they overcame the difficulty by titrating to a preliminary end-point and then, after heating the solution, to a second end-point. It is, however, probable that the basic constituents were adsorbed and not occluded because heating would be unlikely to force occluded matter from the crystal lattice. In practice all these effects are interrelated and possible remedies were sought on a common basis.

In order to ascertain if a common trend could be observed, a series of blank runs was carried out using an oxygen flow rate of 4 ml/min for half an hour. The results are shown in Table I. After run (2), the absorber was cleaned thoroughly with dilute acid and then carefully washed with distilled water. Blanks (3) – (5) were then lower than blanks (1), (2) and (6) – (10), indicating that some hydroxyl ions had been removed by an agent other than the acid added during the titration. This was taken as good evidence for surface interactions. These probable surface reactions must take place mainly on the glass surface because very little barium carbonate is precipitated during a series of blank runs. The apparent interaction with a newly cleaned

TABLE I

BLANK BACK-TITRATIONS EXPRESSED IN ml OF 0.12N HYDROCHLORIC ACID

Blank Number	*Titre (ml)*
1	17.32
2	17.34
3	17.20
4	17.20
5	17.22
6	17.34
7	17.36
8	17.40
9	17.38
10	17.30

glass surface was therefore tested. The absorber was cleaned with dilute acid and distilled water and then left filled with baryta solution overnight, to ensure that the postulated reactions had taken place. Blank determinations were carried out for half an hour with an oxygen flow rate of 4 ml/min. The results were only slightly variable (mean 17.7 ml of 0.05*N* hydrochloric acid) but carbon determinations using sucrose as standard turned out to be high and inconsistent (mean carbon content 42.46% for a required theoretical value of 42.11%). This tendency for high results was a new feature, hence the blank values were redetermined under these conditions. The new mean figure (17.20 ml of 0.05*N* acid) was lower than the first and this reduction could account for the high carbon values. The only major change which had taken place between the two sets of blank runs was a partial change in the nature of the surface of the absorber following deposition of barium carbonate. The reduction in the blank value would probably not take place rapidly under routine conditions; further information was provided by the following experiments.

The absorber was washed with dilute acid and distilled water and then allowed to stand overnight filled with baryta so that the system reached equilibrium. A series of alternate blanks and carbon determinations was then carried out under the same conditions. The blank values slowly decreased and the carbon determinations were high when calculated on the first figure and lower, nearer to the theoretical value, when calculated on the second. These results show that surface interactions do take place. Obviously it would be difficult to prevent them altogether and it was considered that the best solution of the problem was to clean the absorber in dilute acid after each experiment. A new series of blank runs was then carried out using this procedure along with all the other refinements which had been introduced previously. The values were still slightly variable, however; the carbon determinations carried out are shown in Table II below: (Blanks to within *ca.* ± 0.06 ml of 0.05*N* acid).

TABLE II

CARBON DETERMINATIONS USING SUCROSE AS STANDARD (42.11% THEORY)

Carbon found	*Error (%)*
42.16	+0.05
41.87	—0.24
41.30	—0.81
41.97	—0.14
42.23	+0.12
42.18	+0.07
41.92	—0.19
42.18	+0.07
41.95	—0.16
41.10	—1.01
42.18	+0.07
42.35	+0.24
41.59	—0.52

These results taken without rejection from a series of successive tests probably represent the maximum accuracy attainable with the method when reasonably simple apparatus and techniques are used. They indicate that the error is significantly greater than that of the gravimetric method. Final confirmation was obtained when a series of organic compounds was analysed (See Appendix).

COMBUSTION APPARATUS

The apparatus is very similar to that previously described[11], *cf.* Fig. 2. It consists of the following items: Pressure head (A), flowmeter (B), scavenging U-tube (C), combustion tube (D), furnace (E) and absorption vessel (F).

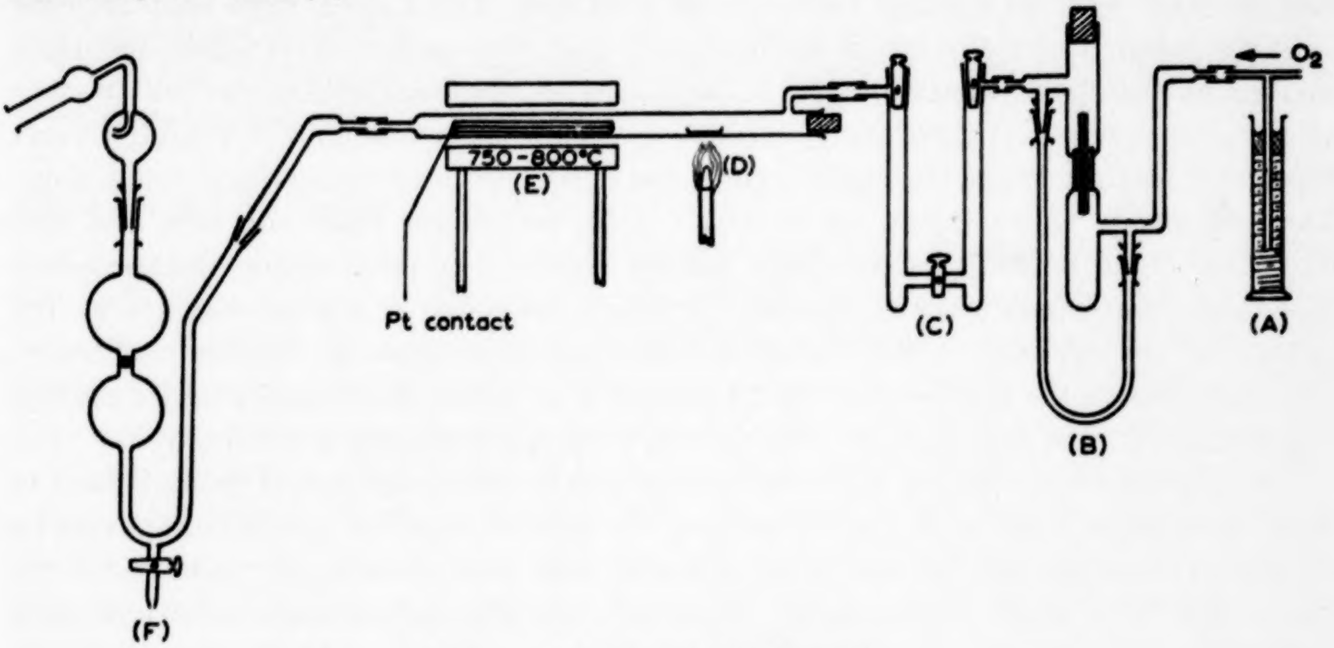

Fig. 2. Line diagram of apparatus.

Mercury is necessary to ensure a sufficient head of pressure behind the sintered plate in the absorber; the scavenging tube is filled with anhydrone and soda asbestos in the usual way. A platinum contact was used in the combustion tube as in the method of FRIEDRICH[12]. Connections were made with impregnated rubber tubing or lubricated standard joints and steel springs. The absorption vessel, illustrated in Fig. 1, was similar to the one used by SCHÖBERL[13] in his method for the determination of sulphur in organic compounds, except that glass beads were not placed below the sinter. The absorber was filled with the absorbent from a burette; half the charge was blown through the sinter with a "blowing bulb" fitted with soda asbestos guard tubes. This bulb was also used as an aid to rinsing the absorber after the combustion.

PROCEDURE

The apparatus was assembled as above with the absorption vessel protected by a guard tube of soda asbestos. The furnace was maintained at 750 – 800° and the oxygen flow was adjusted to 4 ml/min. The samples were combusted in a total of 20 min according to the classical technique[14]. The apparatus was then swept out for 10 min. On completion of a determination, the contents of the absorber were carefully washed into a conical flask with a solution of barium chloride (20% w/v) and the excess alkali was determined by back titration with hydrochloric acid using *o*-cresolphthalein as indicator.

APPENDIX

In a previous paper it was indicated that the main purpose of investigating the titrimetric determination of water and of carbon dioxide was to use these methods for the final measurements in the determination of carbon and hydrogen in organic compounds. Although improved titrimetric methods have been developed as a result of this work, when they were used in place of the gravimetric finish, they were less advantageous. For this reason the results of this very extensive examination have been condensed in the form of an appendix. A more extended account may found elsewhere[15].

The titrimetric finishes were applied to both the "rapid"[16] and the classical "slow"[14] combustion techniques.

"Slow" combustion

The scavenging system and the main combustion furnace are described above. The absorption train consisted of the succinyl chloride reaction vessel, trap and hydrogen chloride absorber as described previously[11], followed by the carbon dioxide absorber as above.

The Friedrich modification was used for the packing of the combustion tube, which consisted of a platinum contact catalyst and a roll of silver gauze. In this method, nitrogen oxides had to

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be removed before the gases entered the water absorber; manganese dioxide powder on 5% platinised asbestos[17] was packed into the beak end of the tube (a layer of 70 mm) and this was maintained at 200° by an auxiliary furnace. Later it was found that a packing of manganese dioxide granules was better than the dispersion of powder on platinised asbestos; the water blanks were then more constant. Manganese dioxide could not be used as an unheated external absorber because some water vapour was absorbed at room temperature.

The combustion of the samples (3-5 mg) was carried out in the usual way over 20 min with the gas flow adjusted to 10 ml/min. The sweep-out time was 40 min. The absorbers were then detached and the back-titration of excess barium hydroxide and the direct titration of hydrochloric acid were done as previously described.

The compounds tested contained oxygen, nitrogen, chlorine, bromine, and sulphur apart from the elements to be determined. Among the results obtained, a consecutive series of 22 determinations showed for the carbon and hydrogen values respectively, an average error of 0.28% and 0.18% and a maximum error of 0.7% and 0.6% (error is understood to be the direct difference from the theoretical value).

"Rapid" combustion

The main apparatus was the same as that described by BELCHER AND INGRAM[16]. At the start of the train, a mercury pressure head had to be inserted to force the gases through the absorbers. The side arm of the combustion tube which contained silver gauze was extended and packed with granules of manganese dioxide maintained by an auxiliary furnace at 200°. The absorption train was the same as for the "slow" combustion.

The combustion of the sample was done in the usual way over 10 min with the gas flow adjusted to 50 ml/min. The sweep-out time was 10 min. The titrations were done as before.

The compounds examined contained the same elements as above. A series of 20 consecutive determinations showed an average error of 0.3% and 0.11%, and a maximum error of 0.95% and 0.35%, for the carbon and hydrogen values respectively.

With both combustion techniques the incidence of errors outside the usual acceptable limits is higher by this titrimetric finish than by the gravimetric finish. The titrimetric method requires much more manipulation and the sweeping-out periods must be lengthened. Possibly the best solution of the problem of avoiding the gravimetric finish would be to explore suitable instrumental methods provided that they would not overcomplicate the apparatus.

ACKNOWLEDGEMENT

We are indebted to the Department of Scientific and Industrial Research for financial aid in respect of this work.

SUMMARY

The titrimetric barium carbonate method for the determination of carbon in organic compounds has been examined and the various sources of error are discussed. The carbon dioxide from the combustion of the sample is absorbed in excess baryta containing 20% (w/v) barium chloride and the excess is back-titrated with hydrochloric acid in the presence of *o*-cresolphthalein indicator.

The value of this method in conjunction with the previously described determination of water with succinyl chloride, for the simultaneous determination of carbon and hydrogen is assessed.

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Received February 6th, 1958

THE APPLICATION OF THIOSALTS IN ANALYSIS

VI. A NEW AND MORE COMPREHENSIVE SCHEME OF QUALITATIVE ANALYSIS

ANALYSIS OF THE INSOLUBLE RESIDUE

by

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The problem of detecting the constituents of an insoluble residue has already been dealt with in a previous publication[1]. In this paper it is proposed to deal with the detection of those additional insoluble compounds and metals that might be present in the residue as a result of including new elements in the "New and more comprehensive scheme of qualitative analysis"[2]. It was found that the inclusion of these new insoluble substances required no change in the first three procedures adopted for identifying the insoluble substances. Only the last prodecure involving fusion with NaOH, Na_2CO_3 and KNO_3 had to be modified in order to provide for the detection of the new compounds. Before discussing the modified procedure for the detection of the new insoluble substances, a brief review of their properties, which are not generally known and which are utilized in their detection is necessary.

Iridium

Iridium metal is insoluble in acids but on fusion with NaOH, K_2CO_3 and KNO_3 it is converted into IrO_2 which is insoluble in water or $1N$ K_2CO_3 solution. IrO_2, however, dissolves in aqua regia and will therefore accompany the alkaline earths in the analysis of the insoluble residue after fusion with alkalies.

Rhodium

Rhodium metal behaves like iridium towards acids but remains unaffected on fusion with alkalies. This metal will, therefore, accompany CeO_2 and ThO_2 after fusion with alkalies. On fusion with potassium hydrogen sulphate, metallic rhodium is converted into rhodium sulphate and can be separated from cerium and thorium by precipitation with sodium sulphide and concentrated hydrochloric acid.

Ruthenium

Ruthenium metal is converted into soluble sodium ruthenate on fusion with alkalies. It can then be separated from the other metals present by precipitation with sodium sulphide.

Tungsten

On treatment with acids in Procedure I[2], metallic tungsten is partially converted into insoluble tungstic acid which passes into solution on boiling the insoluble residue with 4N sodium hydroxide. The metallic tungsten which is not dissolved by sodium hydroxide solution is converted into soluble sodium tungstate on fusion with alkalies and can be easily separated from the other metals by precipitation with mineral acids.

Tantalum and niobium

Tantalum and niobium in the metallic state are not affected by acids in Procedure I[2], nor by boiling with 4N sodium hydroxide solution. Only fusion with alkalies converts them into potassium tantalate and niobate, respectively, which remain in solution in 1N K_2CO_3 solution.

The behaviour of strongly ignited Ta_2O_5 and Nb_2O_5 is exactly the same as that of the metals in the analysis of the insoluble residue.

Fluorides

Although fluorides of lanthanum, yttrium, scandium and rare earths dissolve more or less when freshly precipitated, they are rendered sparingly soluble on strong ignition and can thus be found in the insoluble residue after the standard acid treatment outlined in Procedure I[2]. Although not affected by boiling with 4N sodium hydroxide solution, they are completely decomposed by fusion with alkalies, forming soluble sodium fluoride and insoluble oxides. All these oxides thus formed dissolve on treatment with aqua regia with the exception of ceric oxide. From this solution the lanthanum, yttrium, scandium and rare earths are separated as usual by means of oxalic acid and cerium is converted to ceric sulphate by fusion with potassium hydrogen sulphate.

The behaviour of thorium and calcium fluorides has already been discussed in a previous publication[1].

Phosphates

Freshly precipitated phosphates of lanthanum, yttrium, scandium and rare earths are soluble even in dilute hydrochloric acid but they become practically insoluble in mineral acids after strong ignition. The ignited phosphates are therefore apt to be present in the insoluble residue left after the standard acid treatment. They can be decomposed only on fusion with alkalies, whereby soluble sodium phosphate and insoluble oxides are formed and can then be tested for, as in the case of insoluble fluorides.

Thus the insoluble residue left after the standard acid treatment may contain the following substances in addition to those given in the previous paper[1].

Halides. ScF_3, YF_3, LaF_3 along with the rare-earth fluorides.

Phosphates of Sc, Y, La and other rare earths.

Oxides. Ta_2O_5 and Nb_2O_5.

Metals. W, Ta, Ru, Nb, Ir and Rh.

After treating the insoluble residue with ammonium acetate, 4N sodium hydroxide and ammonium hydroxide solution in Procedures I, II and III of the previous scheme[1], any residue still left may contain the following:

Sulphates. $BaSO_4$, $SrSO_4$, $Cr_2(SO_4)_3$(anhydrous).

Halides. CaF_2, ThF_4, ScF_3, YF_3, LaF_3 and the rare-earth fluorides.

Phosphates of Zr, Ti, Th, Ce, Sn, Sc, Y, La and other rare earths.

Oxides of Al, Cr, Sn, Sb, Si, Zr, Ti, Ce, Th, Ta and Nb.

Metals. W, Ta, Ru, Nb, Ir and Rh.

TABLE I

$BaSO_4$	→	$BaCO_3$	+	Na_2SO_4		$NaAlO_2$		←	Al_2O_3
$SrSO_4$	→	$SrCO_3$	+	Na_2SO_4		Na_2CrO_4		←	Cr_2O_3
$Cr_2(SO_4)_3$	→			Na_2SO_4	+	Na_2CrO_4			
CaF_2	→	$CaCO_3$	+	NaF		Na_2SnO_3		←	SnO_2
ThF_4	→	ThO_2	+	NaF			Na_2ZrO_3	←	ZrO_2
YF_3	→	Y_2O_3	+	NaF		Na_3SbO_4		←	Sb_2O_4
ScF_3	→	Sc_2O_3	+	NaF		$(Na_2TiO_3$	$+ TiO_2)$	←	TiO_2
LaF_3	→	La_2O_3	+	NaF			CeO_2	←	CeO_2
Rare-earth fluorides	→	M_2O_3	+	NaF		Na_2SiO_3		←	SiO_2
ZrP_2O_7	→	Na_2ZrO_3	+	Na_3PO_4		Na_2WO_4		←	W
TiP_2O_7	→	$(TiO_2$	+	$Na_2TiO_3)$	+	Na_3PO_4			
CeP_2O_7	→	CeO_2	+	Na_3PO_4		Na_2RuO_4		←	Ru
SnP_2O_7	→			Na_2SnO_3	+	Na_3PO_4			
ThP_2O_7	→	ThO_2	+	Na_3PO_4			IrO_2	←	Ir
Rare-earth phosphates	→	M_2O_3	+	Na_3PO_4			Rh	←	Rh
Ta	→			$K_8Ta_6O_{19}$				←	Ta_2O_5
Nb	→			$K_8Nb_6O_{19}$				←	Nb_2O_5

(M stands for a rare earth)

TABLE II

<table>
<tr><td colspan="2">Ppt.: $WO_3 \cdot H_2O$ and Ta_2O_5. Treat the ppt. with NaOH solution and filter.</td><td colspan="5">Filt.: Chlorides of Ru, Nb, Ti, Al, Cr, Sb and Sn. Treat with 4*N* NaOH solution to neutralize the large excess of the free acid, keeping the solution still acidic and then with 2*N* Na_2S reagent followed by 4–5 g of CH_3COONH_4. Filter.</td></tr>
<tr><td rowspan="4">Ppt.: Ta_2O_5. Dissolve in $(COONH_4)_2$ and 1*N* H_2SO_4. Test with tannin. A yellow ppt. shows **Ta**</td><td rowspan="4">Filt.: Na_2WO_4. Add Zn and HCl. Blue coloration shows **W**</td><td colspan="4">Ppt.: Ru_2S_3, $Nb(OH)_5$, $Ti(OH)_4$, $Cr(OH)_3$, and $Al(OH)_3$. Treat with dil. HCl and filter.</td><td rowspan="4">Filt.: Thiosalts of Sb and Sn. Test as usual. **Sb, Sn**</td></tr>
<tr><td rowspan="3">Ppt.: Brown Ru_2S_3, shows **Ru**</td><td colspan="3">Filt.: Chlorides of Nb, Ti, Cr, and Al. Treat with NaOH, Na_2O_2 and Na_2CO_3. Boil to decompose Na_2O_2 and filter.</td></tr>
<tr><td colspan="2">Ppt.: $Ti(OH)_4$, $Nb(OH)_5$. Boil with concd. HNO_3, dilute with an equal vol. of water and filter.</td><td rowspan="2">Filt.: Na_2CrO_4 and $NaAlO_2$. Test as usual. **Cr, Al**</td></tr>
<tr><td>Ppt.: Nb_2O_5. Dissolve in $(COONH_4)_2$ and 1*N* H_2SO_4. Test with tannin and CH_3COONH_4. An orange ppt. shows **Nb**</td><td>Filt.: $TiCl_4$. Test as usual. **Ti**</td></tr>
</table>

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Procedure IV

Fuse the residue still left with a large excess of a fusion mixture consisting of NaOH, K_2CO_3 and KNO_3 in a nickel crucible over a blow-pipe flame.

The changes which will be brought about on such fusion may be represented conveniently as in Table I.

(a) Crush and digest the fused mass with 1*N* K_2CO_3 solution (to keep niobium and tantalum in solution), when all the compounds enclosed within the lines will pass into solution. Filter and divide the filtrate into two parts.

(i) Test for phosphate, sulphate, fluoride and silicate.

(ii) Test for W, Ta, Ru, Nb, Ti, Al, Cr, Sb and Sn, see Table II.

(Potassium titanate dissolves only partially in 1*N* K_2CO_3 solution, a major portion is hydrolysed with the precipitation of hydrated titanium oxide.)

Make the solution strongly acid with concd. HCl, boil and filter.

(b) Boil the residue not dissolved by 1*N* K_2CO_3 solution with concd. HCl and concd. HNO_3 in proportion of 5:1. Evaporate to dryness. Take up the residue with dil. HCl and filter (Table III).

TABLE III

<table>
<tr><td rowspan="4">Ppt.: ThO_2, CeO_2 and Rh-oxide.</td><td colspan="4">Filt.: Chlorides of Ir, Zr, Ti, Th, Sc, Y, La, rare earths, Ba, Sr, Ca and Ni (from nickel crucible). Treat with 2<i>N</i> Na_2S in excess followed by CH_3COONH_4 and Na_2CO_3. Filter.</td></tr>
<tr><td colspan="3">Ppt.: NiS and hydroxides of Zr, Ti, Th, Sc, Y, La, rare earths, Ba, Sr and Ca. Treat with cold 1<i>N</i> HCl and filter.</td><td rowspan="3">Filt.: Thiosalt of Ir and Ni. Test as usual.</td></tr>
<tr><td rowspan="2">Ppt.: NiS. Reject.</td><td colspan="2">Filt.: Chlorides of Zr, Ti, Th, Sc, Y, La, rare earths, Ba, Sr and Ca. Dilute to adjust the concentration of acid at 0.5<i>N</i>, add a saturated solution of oxalic acid in excess to the hot solution and filter.</td></tr>
<tr><td>Ppt.: Oxalates of Th, Sc, Y, La and rare earths. Test as usual.</td><td>Filt.: Chlorides and oxalates of Ba, Sr, and Ca. Test as usual.</td></tr>
</table>

Procedure V

The insoluble residue obtained in Procedure IV after treatment with aqua regia may contain Rh, ThO_2 and CeO_2. Fuse with $KHSO_4$ in a silica crucible in order to convert them into sulphates. Dissolve the fused mass in dil. HCl. Treat with 2*N* Na_2S reagent in excess followed by a large excess of concd. HCl and 10–15 g of ammonium acetate (solid). Boil to precipitate Rh completely as Rh_2S_3 and filter (Table IV).

TABLE IV

Ppt.: Brown Rh_2S shows **Rh**	Filt.: Chlorides of Th and Ce. Test as usual[2]. **Th,Ce**

SUMMARY

Modified procedures have been given to provide for the detection of some additional insoluble substances in the more comprehensive scheme of qualitative analysis.

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Received January 6th, 1958

INDIRECT COMPLEXOMETRIC TITRATION OF POTASSIUM, RUBIDIUM, CESIUM, THALLIUM AND AMMONIUM

by

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Most of the methods for the determination of potassium, rubidium, and cesium are gravimetric and involve time-consuming steps of filtering, drying and weighing. In an earlier[1] communication, SEN has described procedures for titrimetric determination of sodium and potassium with EDTA following the precipitation of sodium as sodium zinc uranyl acetate and potassium as potassium sodium cobaltinitrite. Subsequent investigations have shown that sodium silver cobaltinitrite is a much superior precipitating agent for potassium, rubidium and cesium. Thallium(I) and ammonium ions are also quantitatively precipitated under similar conditions. Procedures for the determination of these cations are described here. The final EDTA titration of cobalt which serves to measure the precipitated cation is very accurate and precise. It is quite obvious that the ultimate accuracy and precision of the method is dependent on the initial precipitation of these ions. It is possible to quantitatively precipitate 20 μg of potassium, rubidium, cesium and thallium from 1 ml solution by the procedure described. An ultramicro procedure for the determination of microgram quantities of these elements will be published shortly.

ADIE AND WOOD[2] first used sodium cobaltinitrite as a reagent for potassium, and SHEDD[3] used the reagent for the quantitative determination of potassium. BOWSER[4] increased the sensitivity of the method by precipitating in presence of ethanol. Rubidium and cesium cobaltinitrites were reported by ROSENHEIM AND KOPPEL[5] and they also studied their composition. BUGESS AND KAMM[6] found that sensitivity is increased by precipitating in presence of 0.01N silver ions. ROBINSON AND PUTNUM[7] described a procedure for precipitating 1 mg of potassium from 1 ml of solution using silver cobaltinitrite as the precipitating agent. These authors also described a method for preparing silver cobaltinitrite reagent. Recently[8] potassium silver cobaltinitrite has been used for eventual colorimetric determination of potassium.

In the present work potassium, rubidium, cesium, thallium and ammonium were precipitated as $M_2Ag[Co(NO_2)_6]$ and cobalt was titrated with EDTA as described by SEN[1]. The experimental results conformed with the above composition of the precipitate.

EXPERIMENTAL

All the chemicals used were of analytical reagent grade.

Sodium silver cobaltinitrite reagent

25 g sodium cobaltinitrite prepared according to CUNNINGHAM AND PERKIN[9], was dissolved in

150 ml of water containing 50 g sodium nitrite. To this was added with stirring 2 g of silver nitrate dissolved in 5 ml of water. The solution was diluted to 200 ml and 2 ml of glacial acetic acid was added. The cold solution was aspirated rapidly for 5 min and allowed to stand 48 h in the refrigerator at 4–6° and then filtered by suction using a Whatman-42 filter paper. The solution was stored in a refrigerator. The reagent solution was taken out only during the use and was kept in a cold bath during use and returned to the refrigerator immediately after use.

Quite contrary to the report by some workers, the present author found the reagent to be perfectly stable for several months under the conditions of use mentioned above. There was a slight precipitation after several weeks which neither interfered with the pipetting of the reagent nor diminished its efficiency.

Standard solutions

EDTA (Di-sodium salt, 0.01*M* and 0.005*M*) solution, potassium chloride, rubidium chloride, cesium sulfate, thallium nitrate, ammonium sulfate.

EDTA solution was prepared by direct weighing and was checked against standard calcium solution. Potassium, rubidium, cesium and thallium salts were dried at 85° for 48 h and weighed to prepare the standard solutions. Ammonium sulfate solution was standardized by evolution and titration.

Wash solution

A 0.5 % solution of acetic acid in water.

TABLE I

Sample	*Amount taken* mg	*Amount found* mg	*Sample*	*Amount taken* mg	*Amount found* mg
KCl	15.05	15.07	Cs_2SO_4	52.88	52.66
		15.07			52.66
		15.15			52.30
		14.99			
				26.44	26.33
	7.53	7.58			26.52
		7.50			26.33
		7.42			
		7.50		2.64	2.66
	1.51	1.52	$TlNO_3$	26.61	26.53
		1.51			27.06
		1.52			26.79
					26.53
RbCl	26.66	26.95			
		26.68	$(NH_4)_2SO_4$	6.61	6.73
		26.68			6.66
					6.66
	13.33	12.95			6.59
		13.10			
	2.67	2.76			
		2.60			

PROCEDURE

The sample solution should have a concentration of about 1 to 2 mg/ml. The sample was placed in a centrifuge tube and equal volume of the reagent solution was added and the mixture allowed to stand for 2–3 h in a refrigerator at 4–6°. Longer standing led to the coprecipitation of reagent which was sometimes difficult to wash out and caused high results. After 3 h, the mixture was centrifuged for 10 min at 5000 r.p.m. The clear supernatant liquid was removed by means of a capillary pipette applying very gentle suction. The precipitate was washed with 1–5 ml (depending upon the amount of precipitate) of ice-cold wash solution. After the addition of each instalment of wash solution the precipitate was stirred up with a thin glass rod and then centrifuged and the washings removed in the same way. Washing was continued until the washing was free from silver, about 5 to 8 washings were sufficient. The precipitate was then transferred into a 250-ml beaker with as little water as possible. The precipitate adhearing to the centrifuge tube was then dissolved by heating in 1-2 ml of water containing a few drops of $5N$ HNO_3 and transferred to the beaker. The whole precipitate was then dissolved by heating in 25-50 ml of water containing 0.5 ml $5N$ HNO_3. The solution was cooled and the pH adjusted to 7-8 with sodium carbonate using a hydrion indicator paper. To the solution was then added 1.5-2 g of ammonium thiocyanate and an equal volume of acetone. The solution was then titrated with standard EDTA solution until the blue color due to cobalt thiocyanate complex was discharged. When the amount of cation being determined was 5 mg or less, the precipitate was not transferred but was dissolved in 5 ml of water and a few drops of nitric acid in the centrifuge tube, the pH adjusted to 7-8, and was titrated with $0.005M$ EDTA as above (Calculation: 1 mole EDTA $\equiv$ 1 mole Co $\equiv$ 2 mole alkali metal). The results are given in Table I.

DISCUSSION

The results indicate very good accuracy and reproducibility. The color of the precipitates varied from yellow to orange and in all cases the precipitate was heavy and crystalline and settled immediately. Although thallium is complexed by EDTA, it did not interfere with the titration of cobalt. There was a slight precipitate due to thallium thiocyanate which also did not interfere with the titration. The precipitate of ammonium silver cobaltinitrite was heavy and highly crystalline and it is expected that the method might be better than the conventional evolution and acidimetric determination of ammonia.

ACKNOWLEDGEMENT

The author expresses his sincere gratefulness to Dr. PHILIP W. WEST, Boyd Professor of Chemistry, Louisiana State University, for making available the facilities of his laboratories and his interest in the work. The author also thanks Dr. ANIL K. MUKHERJI for his helpful criticism.

SUMMARY

A titrimetric method using EDTA for the determination of potassium, rubidium, cesium, thallium and ammonium has been developed. These cations are precipitated as $M_2Ag[Co(NO_2)_6]$ and the blue cobalt thiocyanate complex in acetone-water mixed system is titrated with EDTA. Milligram quantities have been determined in the present work.

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Received January 16th, 1958

THE USE OF ETHYLENEDIAMINETETRAACETIC ACID OR NITRILOTRIACETIC ACID AS MASKING AGENTS IN THE DETERMINATION OF PALLADIUM WITH DIMETHYLGLYOXIME OR QUINALDIC ACID

by

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INTRODUCTION

Palladium is usually determined gravimetrically with dimethylglyoxime in an acid solution. It is reported that only the α form of the three isomeric forms of the reagent completely precipitates and is specific for nickel and palladium[1,2]. The β isomer forms soluble complexes with a number of cations such as zinc, iron, and cobalt. The γ isomer is not specific; it precipitates several metals like nickel, palladium, iron, cobalt, bismuth and copper. WALTON[1] states that palladium cannot be precipitated in the presence of ammonium ions with dimethylglyoxime in neutral or slightly basic solution because of the formation of the more stable palladium(II) tetraammine ion. In the presence of ethylenediaminetetraacetic acid (EDTA), it was found that palladium could be quantitatively precipitated with dimethylglyoxime from ammoniacal solutions, that the interference of the previously listed ions could be eliminated, and that the precipitation could be done in the presence of nickel without strict pH control. Dimethylglyoxime is subject to certain disadvantages as an analytical reagent; it possesses a low solubility in water, and forms precipitates which are difficult to manipulate. Consequently, it was decided also to investigate the use of other masking agents in the determination of palladium with quinaldic acid.

Quinaldic acid is water-soluble and forms precipitates which are of higher molecular weight and more readily filtered than the glyoximates. It has been used for the gravimetric determination of cadmium, copper, iron(III), uranium and zinc as well as the colorimetric determination of iron(II)[2,3]. Quinaldic acid forms many insoluble quinaldates, but in the presence of nitrilotriacetic acid (NTA), only silver and palladium precipitated in any amount as the quinaldates. Iron, copper and zinc quinaldates were only slightly co-precipitated with palladium quinaldate in the presence of NTA. These co-precipitated quinaldates were relatively soluble in dilute hydrochloric acid, and could be removed from the palladium precipitate by washing with dilute hydrochloric acid.

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EXPERIMENTAL

Apparatus and reagents

The pH measurements were performed with a Leeds and Northrup Model 7664 pH Meter which was standardized against buffers.

Dimethylglyoxime solution, 0.01*M*, was prepared by dissolving 1.16 g of the reagent in ethanol and diluting to 1 l with the solvent.

Dimethylglyoxime solution, 0.1*M* was prepared by dissolving 11.6 g of the material in acetone and diluting to 1 l with the solvent.

Quinaldic acid, 0.065*M*, was prepared by dissolving 11.25 g of the material in 500 ml of water through titration with sodium hydroxide to pH 6, and then diluting to 1 l with water.

Nitrilotriacetic acid, 0.1*M*, was prepared by dissolving 19.11 g of the material by the same procedure described for quinaldic acid.

Ethylenediaminetetraacetic acid, 0.1*M* was prepared by dissolving 37.23 g of the disodium salt in water and diluting to 1 l.

Standard palladium solution 0.013*M*, was prepared by dissolving 2.30 g of palladium(II) chloride in dilute hydrochloric acid and diluting to 1 l with water. The solution was standardized by direct precipitation of the palladium as the dimethylglyoxime or quinaldate, and contained 34.3 mg of palladium per 25 ml.

Solutions of the foreign ions, 0.1*M* or 0.01*M*, were prepared by dissolving proper amounts of the nitrate, chloride or sulfate salts.

Qualitative reactions

Qualitative tests were performed to determine which metal ions would form quinaldates in the presence and absence of the masking agents. 2 ml of quinaldic acid were added to 10 ml of a 0.01*M* solution of the metal ion. In another test tube, 3 ml of the NTA solution were added prior to the addition of the quinaldic acid. The pH of the solutions was adjusted with sodium carbonate solution or hydrochloric acid to the acidity required to form precipitate in the first mixture. The pH was measured with a pH paper. A similar procedure was followed for the dimethylglyoxime precipitations, except that larger amounts of the reagents were added. The data are presented in Tables I and II.

TABLE I

IONS PRECIPITATED BY QUINALDIC ACID

Ion	*With NTA*	*Without NTA*
Al(III)	no ppt.	white ppt.
Ag(I)	white ppt.	white ppt.
Au(III)	no ppt.	yellow ppt.
Cd(II)	no ppt.	white ppt.
Co(II)	no ppt.	yellow-white ppt.
Cr(III)	no ppt.	gray ppt.
Cu(II)	no ppt.	blue-white ppt.
Fe(II)	no ppt.	yellow ppt.
Fe(III)	no ppt.	yellow ppt.
Hg(I)	no ppt.	white ppt.
Hg(II)	no ppt.	white ppt.
Ni(II)	no ppt.	white ppt.
Pb(II)	no ppt.	white ppt.
Pd(II)	white ppt.	white ppt.
Th(IV)	no ppt.	white ppt.
U(VI)	no ppt.	white ppt.
Zn(II)	no ppt.	white ppt.

TABLE II

IONS PRECIPITATED BY DIMETHYLGLYOXIME

Ion	*With EDTA*	*Without EDTA*
Bi(III)	yellow ppt.[a]	yellow ppt.[a]
Cu(II)	no ppt.	green ppt.[a]
Ni(II)	no ppt.	red ppt.
Pd(II)	yellow ppt.	yellow ppt.

[a] pH 8 or above.

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Properties of the palladium dimethylglyoxime and palladium quinaldate precipitates

It was found that both precipitates were not decomposed by drying overnight at 165°. Decomposition occurred at 200°. Precipitates containing less than 50 mg palladium could be dried to constant weight in 1 h at 125°. Both dimethylglyoxime and quinaldic acid formed precipitates containing two moles of the ligand to one mole of palladium, as shown by the following reactions where HDMG and HQA stand for dimethylglyoxime and quinaldic acid, respectively:

$$\begin{aligned} \mathrm{Pd(II)} + 2\ \mathrm{HDMG} &\rightarrow \mathrm{Pd(II)DMG_2} + 2\ \mathrm{H^+} \\ \mathrm{Pd(II)} + 2\ \mathrm{HQA} &\rightarrow \mathrm{Pd(II)QA_2} + 2\ \mathrm{H^+} \end{aligned}$$

The precipitates were relatively insoluble in most organic reagents. Both precipitates could be dissolved in concentrated ammonium hydroxide, sodium hydroxide, hydrochloric acid and cyanide solutions. The quinaldate precipitate can also be dissolved in thiosulfate and thiocyanate solutions.

Effect of pH, ammonia and foreign anions on the precipitation

It was found that precipitation was complete up to pH 8 with dimethylglyoxime and pH 6.5 with quinaldic acid. In order to mask the interference of foreign ions with EDTA and NTA, it is best to precipitate the palladium above pH 4. The analytical determinations were usually performed at pH 5.5. In the presence of EDTA, palladium could be precipitated from ammoniacal solutions up to pH 8 with dimethylglyoxime. Ammonia and EDTA interfered in the precipitation of palladium with quinaldic acid since these reagents complexed some of the palladium and prevented quantitative precipitation. Nitrate, phosphate, sulfate, tartrate, citrate, carbonate, fluoride and chloride ions caused no interference; but cyanide, thiosulfate, and thiocyanate would interfere.

Recommended gravimetric procedure

Adjust the volume of the solution containing from 15 to 150 mg palladium to 200 ml. Add from 1 to 10 or more ml of the masking agent, depending on the amount of interfering ions that are present. Adjust the acidity of the solution to pH 5.5 with sodium carbonate solution, or hydrochloric acid and heat between 60° to 70°. Add dropwise from a buret at least 20% excess of the amount of the reagent solution necessary for complete precipitation. Digest the precipitate for 30 to 45 min at the same temperature. Filter the precipitate while still warm through a medium porosity sintered-glass crucible, wash 3 to 5 times with 10 ml of $0.1N$ hydrochloric acid, and then wash with sufficient water to remove all traces of the hydrochloric acid. Dry the precipitate to constant weight at 125°. The weight of palladium present in the palladium dimethylglyoxime precipitate is calculated by multiplying the weight of the precipitate by 0.3167. The gravimetric factor for palladium in palladium quinaldate is 0.2366. The results of the analyses and the sample compositions are shown in Table III.

TABLE III

GRAVIMETRIC DETERMINATION — DIMETHYLGLYOXIME PROCEDURE AT pH 5.5

Foreign ions	*ml of 0.01M each ion added*	*ml of 0.1M EDTA added*	*mg of palladium present*	*mg of palladium found*	*Difference mg*
—	—	—	34.3	34.3	0.0
—	—	5.0	34.3	34.2	—0.1
—	—	5.0	34.3	34.3	0.0
—	—	5.0	34.3	34.2[a,b]	—0.1
Cu, Ni	15.0	5.0	17.2	17.3	+0.1
Co, Cr, Fe, Pb	10.0	6.0	17.2	17.5	+0.3
Fe, Ni	6.0	8.0	34.3	34.1	—0.2
Al, Cd, Co, Cr, Cu, Hg, Mn, Pb, Zn	10.0	12.0	34.3	34.3	0.0
Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	10.0	13.0	34.3	34.4	+0.1
Fe, Ni[a]	100.0	24.0	34.3	34.1	—0.2
Fe, Ni[a,b]	100.0	24.0	34.3	34.1	—0.2
Fe, Ni[a,b]	100.0	24.0	34.3	34.4	+0.1
Ce, La, Nd, Gd, Pr, Sm, Yb, U, Zr	1.0	10.0	68.6	68.4	—0.2
Ir, Os	1.0	1.0	155.4	155.3	—0.1
Rh, Ru	1.0	1.0	155.4	155.5	+0.1

[a] Precipitated at pH 8.

[b] Containing 2.5 g of ammonium chloride.

TABLE III (continued)

GRAVIMETRIC DETERMINATION — QUINALDIC ACID PROCEDURE AT pH 5.5

Foreign ions	*ml of 0.01M each ion added*	*ml of 0.1M NTA added*	*mg of palladium present*	*mg of palladium found*	*Difference mg*
Ru, Rh, Os, Ir	5.0	4.0	17.2	17.5	+0.3
U, Th, Bi	5.0	4.0	17.2	17.0	—0.2
—	—	—	34.3	34.3	0.0
Al, Cd, Cr, Hg, Mn, Ni	10.0	7.0	34.3	34.4	+0.1
Al, Cd, Cr, Hg, Mn, Ni	10.0	7.0	34.3	34.5	+0.2
Fe, Cu, Zn	20.0	7.0	34.3	34.3	0.0
Fe, Cu, Zn	20.0	7.0	34.3	34.3	0.0
Fe, Cu, Zn	20.0	8.0	34.3	34.3	0.0
Al, Ni, Mn	50.0	30.0	68.6	68.4	—0.2
Co, Cd	100.0	30.0	68.6	68.5	—0.1
La, Nd, Gd, Pr, Sm, Yb	1.0	0.8	155.4	155.4	0.0
Pt, Zr, Ir	10.0	3.5	155.4	155.6	+0.2

DISCUSSION

The results of the determination of palladium in the presence of normally interfering ions are presented in Table III. Of the ions tested, only gold was found to interfere. In both procedures, the complexing agents reduced gold to the metallic state prior to the addition of the precipitating agent and some palladium was probably co-precipitated with the gold as the results were low in subsequent palladium analyses. If small amounts of bismuth were present in the determination of palladium with dimethylglyoxime, no interference was evident. If more than 20 mg bismuth were present in the sample, incomplete precipitation of the palladium was observed. This interference could be eliminated by the addition of tartrate prior to the pH adjustment. However, no interference by bismuth was observed in the determination of palladium with quinaldic acid. It has been reported that dimethylglyoxime forms a precipitate with cobalt and ferric iron when both are present in the same solution[4,5]. In the presence of EDTA, this interference was not observed as EDTA probably prevented the formation of all precipitates with dimethylglyoxime except palladium. When samples contained chloride ions, addition of silver ions formed silver chloride.

The amounts of the reagents used in both procedures were not critical as long as an excess was present. Sufficient amounts of EDTA and NTA must be used to prevent precipitation of the foreign ions either as the hydroxides, glyoximates, or quinaldates. The adjustment of the pH of the solution is not critical prior to the precipitation, as the precipitation can be made in the range from pH 4 to 6. Sodium hydroxide and sodium phosphate as well as sodium carbonate served for pH adjustment. Dimethylglyoxime was dissolved in both acetone and ethanol for the precipitation of palladium. The acetone solution was found to be preferable because of the higher solubility of dimethylglyoxime in acetone. The drying temperature is not critical and both palladium precipitates could be dried overnight at 125° without decomposition. At 170°, slow decomposition of both precipitates was observed.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to ALEX J. SANTORO for preliminary investigations on the problem, and to WALTER T. SCHRENK for his interest. They also wish to express their thanks to the Research Corporation for an F. Gardner Cottrell grant to support this work.

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SUMMARY

The use of complexing agents to mask interference in the gravimetric determination of palladium has been studied. Ethylenediaminetetraacetic acid was used to complex interfering ions in the determination of palladium with dimethylglyoxime, and nitrilotriacetic acid has been employed as a masking agent in the determination of palladium with quinaldic acid. From 15 to 150 mg of palladium were determined. All the metals tested do not interfere with the exception of gold which is reduced by the complexing agents and has to be removed prior to the determination. The procedures are rapid, simple and accurate.

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Received February 10th, 1958

ERIOCHROME BLACK A AS AN INDICATOR FOR CHELATOMETRIC TITRATIONS

by

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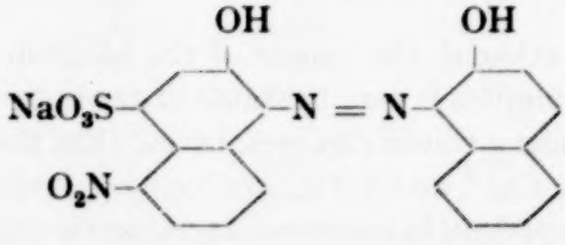
Eriochrome Black T was the first complexometric metal indicator to be recommended on the basis of the high stability of its magnesium complex.

SCHNEIDER AND EMMERICH[1] employed Eriochrome Blue Black B in ethylenediaminetetraacetic acid (EDTA) titrations of calcium and magnesium in syrups and solutions.

CHENG[2] reported the use of Eriochrome Blue Black R under the trivial name Zinchrome for the determination of water hardness.

The present work describes the use of Eriochrome Black A for analytical purposes. It is the sodium salt of 4-sulpho-5-nitro-2-hydroxy-α-naphthalene-azo-β-naphthol and will be designated as Erio A for short. The structure of the dye is as follows:



Properties of Erio A

Erio A is a brownish black powder with a faint metallic lustre, soluble in water and in ethanol giving a dark blue solution. In acidic solutions the dye polymerizes forming a brown product. The aqueous solutions of the dye attain a blue colour at pH 7 to 10 and above pH 10 the colour turns to violet-red. The blue colour obtained remains unchanged on boiling. Thus it seems that Erio A will find no application in complexometric titrations in acid media. The aqueous and ethanolic solutions of the dye are stable for a few days; however if the solution is kept for a period of more than a week, the colour gradually changes and after about two weeks it turns completely brown because of polymerization.

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Erio A metal complexes

The metal complexes of Erio A are easily prepared by adding a few drops of a freshly prepared aqueous solution of the dye to solutions of heavy metals. Experimental results indicated that red chelate compounds were formed regardless of the nature of the anions present, when the pH of the solution was maintained within the range of 8 to 10. The cations that caused a colour change with the dye are listed in Table I. Spot tests were made by mixing a micro drop (0.015 ml) of the metal solution with a micro drop of an aqueous 1% solution of the dye at pH 10.

Results and remarks on spot tests

The results in Table I show that the blue colour of Erio A turns pink, red, or rose on the addition of the ions indicated in the Table. Strontium formed a red lake with the dye, which dissolved in ethanol, the colour of the solution turning blue, indicating that the strontium-dye complex is very unstable in alcoholic solutions. The sensitivity limits of the reactions causing colour changes, reveal that the presence of Zn^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Mg^{+2}, Pb^{+2}, Cu^{+2} and Cd^{+2} ions can be easily detected when minute amounts of these ions are present in solutions, and that the reaction may be applied to the detection of the end-points of titrations of these metals with EDTA solutions.

TABLE I

COLOUR REACTIONS OF METALLIC IONS WITH ERIO A

Ion	*Colour*	*Identification limit μg*	*Dilution limit*
Zn	pink	0.01	$1 : 2 \cdot 10^6$
Cu	red	0.02	$1 : 2 \cdot 10^6$
Pb	red	0.003	$1 : 1 \cdot 10^7$
Cd	rose	0.22	$1 : 33 \cdot 10^6$
Mn	rose	0.01	$1 : 2.5 \cdot 10^6$
Ni	red	0.02	$1 : 2 \cdot 10^6$
Co	red	0.083	$1 : 5.8 \cdot 10^6$
Mg	red	0.54	$1 : 41 \cdot 10^3$
Ca	red	not sensitive	
Sr	red (unstable)		
Ba	insoluble red lake		

Applications

The use of Erio A as a metal indicator in EDTA titrations has been investigated. The ions chosen for this purpose were Zn^{+2}, Mn^{+2}, Ni^{+2}, Cu^{+2} and Pb^{+2}, because of the reversibility and sensitivity of the colour change they cause with the indicator. Although Erio A is not a specific reagent for a certain cation, yet it is evident that polyvalent cations can be determined colorimetrically after their separation by the usual analytical methods. These colorimetric procedures will be published elsewhere.

DETERMINATION OF METAL IONS

Reagents

Indicator powder. 0.1 g of Eriochrome Black A was ground with 10 g of sodium chloride (A.R.).

EDTA solution 0.01M. Dissolve 3.722 g of reagent grade disodium ethylenediaminetetraacetate dihydrate in water; dilute to 1 liter with bidistilled water.

Buffer solution. Dissolve 13.5 g of ammonium chloride in water, add 88 ml of concentrated ammonia and dilute with water to 250 ml.

Metal salt solution. Prepare 0.01 *M* solutions of the various metals from analytical grade reagents. Standardize these solutions against EDTA using Eriochrome Black T or murexide as indicator according to the usual procedures for the determination of the appropriate cation.

Other reagents. Ascorbic acid, Rochelle salt or tartaric acid, Eriochrome Black T indicator powder.

Procedures

Determination of zinc. Pipette an aliquot portion of the sample solution in a conical flask, add about 1 ml of the buffer for each 10 ml of the sample solution. Add about 3 mg of Erio A powder and titrate with 0.01 *M* EDTA solution until the colour changes from red to clear blue. 1 ml EDTA (0.01 *M*) is equivalent to 0.6538 mg Zn.

Determination of manganese. To an aliquot portion of the sample solution of manganese, add a few mg of ascorbic acid, 1 ml of the buffer and about 3 mg of the indicator powder and titrate with EDTA in the cold. 1 ml 0.01 *M* EDTA solution is equivalent to 0.5493 mg Mn.

TABLE II

EDTA TITRATIONS OF SOME METALS USING ERIO A AS INDICATOR

Metal ion	*mg metal*			*ml 0.01M EDTA*		
	present	*found*	*error*	*calculated*	*consumed*	*error*
Zn	0.785	0.785	0.00	1.20	1.20	0.00
	1.673	1.661	—0.012	2.56	2.54	—0.02
	3.693	3.713	0.020	5.65	5.68	0.03
	6.001	5.988	0.013	9.18	9.16	—0.02
Mn	0.468	0.461	—0.007	0.85	0.84	—0.01
	0.780	0.785	0.005	1.42	1.43	0.01
	2.076	2.071	—0.005	3.78	3.77	—0.01
	5.482	5.482	0.00	9.98	9.98	0.00
Ni	0.234	0.246	0.0118	0.40	0.42	0.02
	0.376	0.387	0.011	0.64	0.66	0.02
	0.781	0.786	0.005	1.33	1.34	0.01
	1.514	1.503	—0.011	2.58	2.56	—0.02
Cu	0.394	0.382	—0.012	0.60	—0.60	—0.02
	0.953	0.953	0.00	1.50	1.50	0.00
	1.387	1.372	—0.015	2.18	2.16	—0.02
	2.262	2.243	—0.019	3.56	3.53	—0.03
Pb	1.036	1.077	0.041	0.50	0.52	0.02
	3.067	3.067	0.00	1.48	1.48	0.00
	7.459	7.439	0.020	3.60	3.59	—0.01
	16.370	16.328	—0.042	7.90	7.88	—0.02

Determination of nickel. To an aliquot portion of nickel solution, add 1 ml buffer. If the solution becomes deeply coloured, dilute with distilled water. Add the indicator powder, heat nearly to boiling (about 80°) and titrate with 0.01 *M* EDTA solution, while hot, to a clear change of violet to blue. 1 ml EDTA (0.01 *M*) is equivalent to 0.5869 mg Ni.

Determination of copper. Proceed as in the determination of nickel. 1 ml 0.01 *M* EDTA is equivalent to 0.6357 mg Cu.

Determination of lead. To an aliquot portion of the lead solution, add a few mg of tartaric acid, adjust the pH by adding the buffer; add the indicator powder and titrate with 0.01 *M* EDTA to a clear colour change of red to blue. 1 ml 0.01 *M* EDTA solution is equivalent to 2.0721 mg Pb.

RESULTS AND DISCUSSION

The results of the representative determinations of the metals given indicate that satisfactory analytical values have been obtained by the given procedures for the various metals. The titration of most of these metals could be easily carried out in the cold, a sharp end-point being obtained. The experimental error calculated from the results of a large number of titrations was very small, indicating the high accuracy and precision of the procedures when using Erio A as indicator. These errors were of the magnitude of the usual error in titrimetric procedures, corresponding to the size of half a drop of the titrant, the minimum perceptible volume in such titrations.

In the titration of manganese there was no need to use either magnesium complexonate or to add tartaric acid as described by FLASCHKA[3]. The presence of ascorbic acid was quite sufficient to prevent the precipitation of any hydrated manganic oxide; moreover, the titration was readily done in the cold, and the end-point was very sharp.

In contrast to Erio T, Erio A proved to be a suitable indicator for the detection of both nickel and copper when the titrations were done at elevated temperatures (70–80°). The sensitivity of the colour change is increased on diluting nickel or copper solutions. Addition of tartaric acid was necessary in the determination of lead to prevent the precipitation of lead hydroxide by the effect of the buffer; in this case the titration was carried out in the hot solution, otherwise the end-point is only reached after using a slight excess of EDTA.

SUMMARY

The use of Eriochrome Black A for the EDTA titrations of Zn, Mn, Ni, Pb and Cu ions is described. Spot tests for the determination of the sensitivity limits of detection have been made.

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Received March 1st, 1958

GRAVIMETRIC DETERMINATION OF IRON WITH BENZENEPHOSPHINIC ACID

by

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The use of benzenephosphinic acid for the gravimetric determination of iron has been proposed by BANKS AND SKOOG[1]. These authors found the reagent to be quite satisfactory for quantities of iron greater than 60 mg. With smaller amounts they encountered a systematic negative error caused by the solubility of the ferric benzenephosphinate in the wash water. It therefore appeared advisable to try to adapt the method to a micro scale of work in which the volume of solution used would be considerably smaller. This has been done and, further, the behavior of ferric benzenephosphinate as a function of temperature has been studied.

EXPERIMENTAL

Reagents

Solutions of ferric iron were prepared from analytically pure iron wire or else from analytica reagent-grade ferrous ammonium sulfate hexahydrate[1]. They were standardized by a number of standard methods.

Aqueous solutions of benzenephosphinic acid were prepared from purified solid. This had been obtained from Victor Chemical Works, Chicago, Ill., U.S.A. To purify it, the solid was placed in a flask, covered with anhydrous diethyl ether and allowed to stand for 24 h with intermittent shaking. The ether was decanted and the process repeated twice. Finally, the solid was separated by filtration and the excess ether was removed under vacuum.

Apparatus

The analyses were carried out in tared test tubes measuring 18 × 60 mm. The precipitates were collected on modified Emich filter sticks, developed at the Laboratory for Microanalysis of the Technological University, Delft, The Netherlands. The filtering medium was finely shredded Powminco asbestos.

The behavior of the precipitate at elevated temperatures was studied with the aid of a thermobalance constructed from ordinary laboratory apparatus. It is shown schematically in Fig. 1. The diagram and accompanying legend are self-explanatory.

Analytical procedure

2 ml of an acidic ferric iron solution containing approximately 1 mg of iron per ml are pipetted into a tared test tube. The solution is warmed to 50° in a water bath and neutralized to a methyl orange end-point with $4N$ ammonia. 1 ml of $2N$ sulfuric acid is added. Sufficient water is added to bring the volume to 4 ml. The solution is heated to 95° in the water-bath. 1 ml of $0.2N$ benzenephosphinic acid is added dropwise with constant stirring. The precipitate is digested for 30 min at 70–80° with intermittent stirring. The solution is then cooled in a refrigerator for approximately 30 min. The precipitate is collected on the filter stick by vacuum filtration from the cold solution and washed with 0.5-ml portions of ice-cold water until free from sulfate. The latter can be confirmed by collecting a 0.5-ml portion in 1 ml of 0.1% barium chloride solution. The solution should remain clear. Ordinarily about six 0.5-ml portions of water are required. The precipitate, filter stick and test tube are dried to constant weight at 100–110°. The weight of iron can be calculated using the gravimetric factor: $\frac{\mathrm{Fe}}{\mathrm{Fe(C_6H_6PO_2)_3}} = 0.1166$.

ANALYTICAL RESULTS AND DISCUSSION

The results of analyses performed with the above procedure are given in Table I. The average deviation of the eight determinations is 0.51%. The ease and rapidity of the procedure is illustrated by the fact that several of the determinations were done by undergraduate students in a single afternoon.

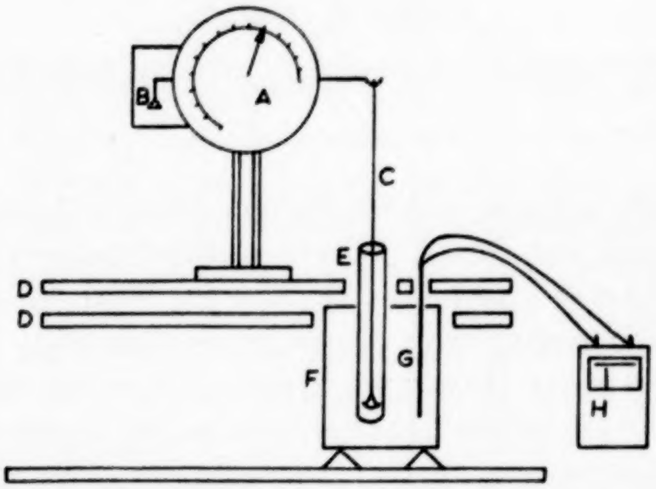

Fig. 1. Schematic diagram of thermobalance. A: Torsion balance of 50 mg capacity. B: Pan for counterpoise. C: Thin platinum wire and platinum sample dish. D: Asbestos insulation. E: Quartz tube, 2 × 20 cm. F: Electric oven. G: Thermocouple with Pt–PtRh element. H: Millivoltmeter calibrated for temperature measurement.

TABLE I

SUMMARY OF IRON DETERMINATIONS

Fe taken *mg*	*Fe found* *mg*	*Relative error*
1.937	1.945	+ 0.46
1.937	1.920	— 0.88
2.018	2.041	+ 1.14
2.018	2.009	— 0.45
1.998	2.000	+ 0.10
1.998	2.006	+ 0.40
2.124	2.134	+ 0.47
2.124	2.118	— 0.28
	Average	0.51

Thermoanalytical behavior of ferric benzenephosphinate

A sample of ferric benzenephosphinate was prepared according to the analytical procedure with the omission of the drying step. Approximately 25 mg were placed in the sample dish of the thermobalance and heated at a rate of about 150°/h. Fig. 2 shows a composite curve constructed from several runs.

At temperatures below 90° the substance loses water in a continuous fashion. Between 90° and 275°, the weight corresponds to ferric benzenephosphinate. This melts with decomposition at a temperature of 275–280°. The relative weight of the decomposition product varies somewhat, probably depending on the amount of oxygen in the neighborhood of the sample dish at the moment of decomposition. The final plateau between 600° and 650° corresponds to the formula FeP_3O_9. Such a compound has been prepared by BRASSEUR[2,3]. Positive identification of the product was beyond the scope of this investigation.

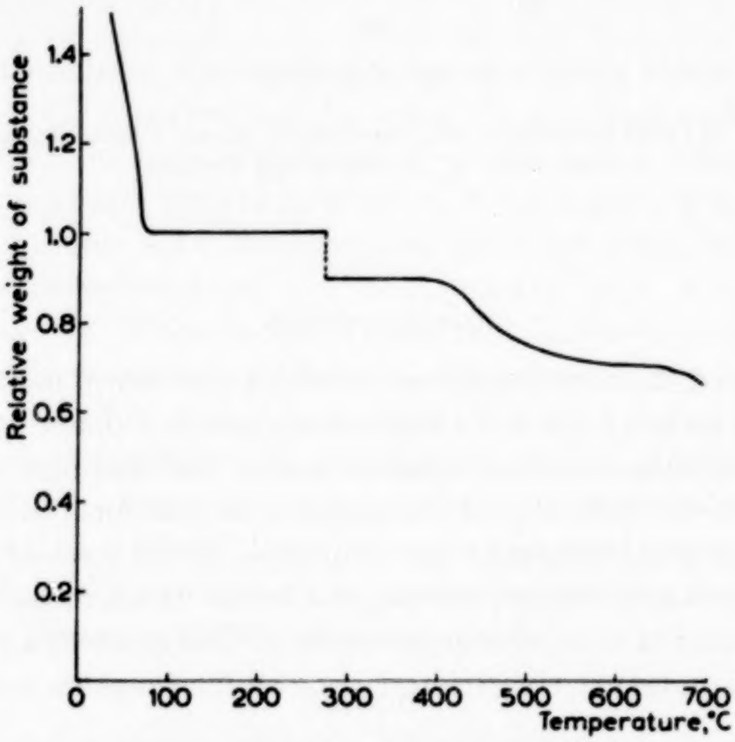

Fig. 2. Thermoanalysis of ferric benzenephosphinate.

CONCLUSIONS

It has been demonstrated that ferric iron in acidic aqueous solution can be quantitatively precipitated by benzenephosphinic acid in amounts as small as 2 mg. The precipitate, $Fe(C_6H_6PO_2)_3$, is stable in the temperature region of 90–275°. The determination on the micro scale is easier and more rapid than that on the macro scale. Furthermore, the systematic error due to solubility in the wash water is reduced. Separations of the ferric ion from other ions have not been attempted on the micro scale, but there is no reason to doubt that they could be accomplished as well as those on the macro scale carried out by BANKS, PENNELL AND SKOOG[4]. Further work on this point is contemplated.

SUMMARY

Benzenephosphinic acid ($C_6H_7PO_2$) can be used to determine as little as 2 mg of ferric iron gravimetrically as ferric benzenephosphinate, $Fe(C_6H_6PO_2)_3$. The latter maintains a constant weight between 90° and 275°. The analytical procedure is given. Results indicate an average deviation of 0.5%.

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Received February 26th, 1958

THE REDUCTION OF HEXAVALENT TUNGSTEN

by

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INTRODUCTION

A study of the interaction of cytochrome c with a number of metallic ions[1] required the preparation of a reduced form of tungsten of definite valency state. The problems encountered in attempting to reduce tungstic acid in acid medium are well known and are due primarily to the difficulty of obtaining a soluble form of tungstic acid.

In this work hexavalent tungsten was employed in the form of WCl_6 which could easily be dissolved in warm ethanol forming a solution which remained clear for a time when hydrochloric acid ($d = 1.18$) was added to it. This enabled a reduction by means of a metal or metal amalgam to be effected while all the tungsten was in a soluble form.

EXPERIMENTAL

Preparation of WCl_6

Tungsten metal powder as supplied by B.D.H. was heated to redness in a porcelain boat in a stream of chlorine (from a cylinder). The gas had been previously dried by passage through sulphuric acid and then through a tube packed with phosphorus pentoxide. These drying precautions were necessary to prevent the formation of $WOCl_4$ in substantial quantities. The steel-blue crystalline sublimate of the hexachloride was removed and, if necessary, re-sublimed in dry chlorine before being stored for use in sealed tubes. Found: W 46.4, Cl 53.5. Calculated for WCl_6: W 46.3, Cl 53.65. Tungsten analyses were carried out by dissolving 700–1500 mg of the compound in a minimum of NaOH solution with a few drops of 100 vol. % H_2O_2 and boiling to decompose the excess of peroxide. The solution was filtered, and the combined filtrate and washings neutralised with nitric acid, an excess of which was added to give a concentration of about 20% v/v in the final solution. After standing for an hour or two the precipitated tungstic acid was filtered* (No. 42 paper moistened with 20% HNO_3), washed with 20% HNO_3, and ignited to WO_3. As a check a separate sample of the hexachloride was dissolved in NaOH solution as before and, after filtration, tungsten was precipitated by the addition of an excess of ethanolic 8-hydroxyquinoline followed by acetic acid to bring the pH of the solution to 3–4[2]. After allowing the mixture to stand overnight the granular precipitate of tungsten oxinate was filtered, washed with ethanol, cold water, hot water and ignited to WO_3. The values for % W found by the two methods were: nitric acid 46.4, oxine 46.5. In view of this, nitric acid precipitation was employed in subsequent tungsten determinations as it avoided the burning off of large amounts of hard carbon during ignition.

All WCl_6 samples contained Fe (presumably as $FeCl_3$), and this was derived from the tungsten powder. The washed residue from the solutions of WCl_6 in NaOH were dissolved in hot 2*N* HCl and the solution diluted to 100 ml. Fe was estimated colorimetrically upon aliquots of the solution by extraction as ferric thiocyanate into amyl alcohol–ether as described in a previous paper[3]. From the values found it was calculated that WCl_6 contained 0.7–1.0% w/w $FeCl_3$ and a corresponding allowance was made in the weights of WCl_6 taken.

Chlorine was estimated by the Mohr titration method as follows: WCl_6 (1100–1200 mg) was dissolved in NaOH with a few drops of H_2O_2 and excess of the latter destroyed by boiling as before. The solution was filtered and diluted to 100 ml. 20-ml aliquots were taken and neutralised (methyl red) with 20% HNO_3. 20 ml of the acid was added in excess and the mixture was allowed to stand for 1–2 h to allow the precipitate of tungstic acid to flocculate. It was then filtered (No. 41 paper moistened with 20% HNO_3) and the residue washed with distilled water. The combined filtrate and washings were neutralised with NaOH (methyl red) and titrated with 0.1N $AgNO_3$ using potassium chromate as indicator. Titre values agreed to within 0.2 ml.

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* If the filtrate was not clear and colourless, it was heated to boiling with a little cellulose powder and, after cooling, the mixture was re-filtered.

Reduction of W^{VI}

It is known that tungsten is not reduced to any definite valency state in the Jones Reductor, but SOMEYA[4] reported that by using Pb amalgam and HCl a quantitative reduction to the trivalent state is obtained in an inert atmosphere.

A number of experiments were carried out in which known weights of W (as WCl_6) were dissolved in ethanol with warming and, after the addition of 10N hydrochloric acid, reduction was carried out at 70°–80° in a stream of CO_2 by the addition of different metallic reducing agents. When excess of reductant had been added and reaction appeared to be complete, water was added and ethanol expelled by boiling the solution in the CO_2 stream. The solution was then cooled, diluted to 100 ml with distilled water, and measured aliquots titrated (CO_2 atmosphere) with 0.01M $KMnO_4$ in a ten fold excess of 5% v/v H_2SO_4. From the titre values the valency states of tungsten in the solution were calculated. „Blank" titrations were also carried out by the same technique, no tungsten being added prior to metal-acid reduction; the titre values so obtained could be neglected. Some results are shown in Table I.

TABLE I

		Reduction medium		*Metal reductant*	*mg W present in 20 ml aliquot*	*0.01M $KMnO_4$ titre ml*	*ml $KMnO_4$ calc. for 100% reduction to*			*% composition calc. on titre value*
		ml EtOH	*ml HCl*				W^{V}	W^{IV}	W^{III}	
A.	(*i*)	5	20	Na Hg	126.3	17.8	13.7	27.4	41.1	W^{IV} 30 W^{V} 70
	(*ii*)	5	20	Na Hg	116.3	19.6	12.7	25.4	38.1	W^{IV} 54 W^{V} 46
	(*iii*)	5	20	Na Hg	117	18.0	12.7	25.4	38.1	W^{IV} 42 W^{V} 58
B.	(*i*)	5	30	Pb Hg	259.1[a]	68.0	28.1	56.3	84.4	W^{III} 42 W^{IV} 58
	(*ii*)	5	50	Pb Hg	147.3[a]	39.5	16.0	32.0	48.0	W^{III} 47 W^{IV} 53
	(*iii*)	15	20	Pb Hg	138.8[a]	24.8	15.1	30.2	45.3	W^{IV} 64 W^{V} 36
C.	(*i*)	5	30	Zn dust	38.3	9.7	4.2	8.3	12.5	W^{III} 33 W^{IV} 67
	(*ii*)	5	30	Zn dust	37.4	9.4	4.1	8.2	12.3	W^{III} 30 W^{IV} 70
D.	(*i*)	15	20	Zn dust	128.4	28.4	14.0	28.0	42.0	W^{III} 3 W^{IV} 97
	(*ii*)	15	20	Zn dust	26.88	6.3	3.0	6.0	9.0	W^{III} 10 W^{IV} 90
	(*iii*)	15	20	Zn dust	63.78	14.2	7.0	14.0	21.0	W^{III} 3 W^{IV} 97

[a] The entire W fraction was titrated because precipitation of $PbCl_2$ prevented accurate dilution to 100 ml.

From the results it appears that the valency of tungsten in the reduced solutions varies according to the conditions in which reduction has taken place. Sodium amalgam gives incomplete reduction to W^{IV} while zinc dust and lead amalgam in the presence of a large excess of hydrochloric acid over ethanol give complete reduction to W^{IV} and a further 30–50% reduction to the trivalent state. Nothing approximating to a complete reduction to W^{III} was obtained with lead amalgam although the mixture used in *B (ii)* was subjected to prolonged boiling in a stream of CO_2. Quantitative reduction to the tetravalent state (using Zn dust) appeared to be approached under the conditions employed in *D*.

Preparation of a Zn-free W^{IV} solution

WCl_6 (1.5–2.0 g) was dissolved in ethanol (15 ml) with warming and 10*N* hydrochloric acid (20 ml) added to the cooled mixture. Zinc dust was added gradually until the colour of the solution was reddish-brown. A stream of CO_2 was passed through the solution which was then boiled gently until the volume had decreased to 10–15 ml. The solution was cooled and water (30 ml) added before filtering (No. 41 paper) into a large flask (500–750 ml) from which air had been displaced by a stream of CO_2. Acetone (300 ml) was added to the flask, which was then stoppered and allowed to stand overnight. The supernatant liquid was withdrawn and the brown precipitate filtered off at the pump (double thickness of No. 42 paper). The solid was thoroughly washed with acetone and ether and dried. It was redissolved in a little cold 10*N* HCl (CO_2 atmosphere), water was added and the mixture filtered and stored under CO_2 in sealed tubes. Spots of the concentrated solution were analysed by downward paper-strip chromatography employing a mixture of acetone, ethanol, and acetic acid (4:2:1) as eluant.

The strips were developed by dipping them into an ethereal solution of oxine and examining them over ammonia in U.V. light. R_F values were 0.0 for W (dark) and 0.6–0.7 for Zn (greenish yellow fluorescence). One precipitation with acetone was usually sufficient to render the compound free from Zn^{+2}, provided the subsequent washing with acetone was thorough. However, if traces of Zn^{+2} were detected, complete removal was effected by a second precipitation.

The above method also freed the tungsten material from Fe in one precipitation. Most of the acetone used for the precipitation and washings was recovered by distillation, collecting the fraction boiling at 58°–62°.

The valency of the tungsten in the Zn-free solution was determined by titrating measured aliquots (in an excess of 5% H_2SO_4) with 0.01*M* $KMnO_4$ (1.58 g/l). The titre values were related to the weight of tungsten present in the aliquots; this was determined by adding nitric acid drop by drop to a separate aliquot of solution with warming until all the tungsten was converted to tungstic acid. The precipitate was allowed to flocculate, filtered (No. 42 paper moistened with 20% HNO_3), washed with 20% HNO_3, and ignited to WO_3. A typical result was:

$$233 \text{ mg } WO_3 \ (\equiv 184.8 \text{ mg W}) \equiv 39.6 \text{ ml } 0.01M \ KMnO_4$$

$$(\text{Calc. for } W^{III} \ 60.0 \text{ ml}, \ W^{IV} \ 40.0 \text{ ml}, \ W^{V} \ 20.0 \text{ ml})$$

To check the efficiency of the gravimetric method, the determination of W was carried out by the nitric acid and oxine procedures on aliquots (30 ml) of another freshly prepared W^{IV} solution. In the oxine method the estimation was completed as described for WCl_6, after oxidising the reduced W with HNO_3 and dissolving the precipitated tungstic acid in an excess of NaOH. The weights of WO_3 obtained from the aliquots by the two methods were: nitric acid 221.4 mg, oxine 221.0 mg, showing agreement to within 0.2% for the two methods.

Composition of the acetone precipitate

This was analysed for W and Cl by the methods used for WCl_6 except that analysis for Fe was omitted as the precipitate was free from this metal. The compound appeared to be of variable composition, with W and Cl contents of 67–69% and 8–10% respectively. The remainder, 21–25%, was presumed to be OH. It is suggested that the solid is a basic chloride of W^{IV} whose composition varies between $W(OH)_{3.5}Cl_{0.5}$ (W 70.7, Cl 6.7, OH 22.7) and $W(OH)_3Cl$ (W 68.0, Cl 13.1, OH 19.0).

Removal of Zn^{+2} from the reduced tungsten solution was also accomplished by means of cellulose column chromatography. The eluants used were (1) HCNS in ether[5] or (2) Acetone–ethanol–acetic acid (4:2:1). Zinc was eluted from the column first by

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these eluants, and an exactly similar technique to that employed for a $Mo^{III}-Zn^{+2}$ separation was used[5], except that it was necessary to displace air from the liquid above the cellulose during the runs to prevent the oxidation of some W^{IV}. The tungsten fractions were found to be free from Zn^{+2} but Fe was still present. Tungsten was not completely removed from the cellulose by elution with water or acid in the cold, and it was necessary to extrude the column and heat the cellulose with $2N$ HCl (in CO_2) to effect this. The filtered tungsten extracts and eluates were combined, 20–30 ml of $10N$ HCl was added and the mixtures concentrated by distillation in a stream of CO_2. A considerable amount of HCNS was present in the distillate from samples prepared with eluant (1). The concentrates were filtered if necessary and evaporated to dryness over P_2O_5 in a desiccator* from which air had been displaced by CO_2 and then exhausted. A lustrous black deliquescent residue, of variable W and Cl content, was obtained. This was readily soluble in water giving a clear brown solution. Aliquots of the concentrated extracts were analysed gravimetrically for W (by HNO_3 oxidation) and titrated in 5% H_2SO_4 solution with $0.01M$ $KMnO_4$ to determine the valency of the tungsten present. If eluant (1) had been used the titre values, although they indicated tetravalency, were unsatisfactory owing to the presence of a little HCNS. The results using eluant (2) were more satisfactory, and two are given below.

(i) 21.52 mg WO_3 ($\equiv$ 170.7 mg W) $\equiv$ 37.1 ml 0.01 $KMnO_4$
(Calc. for W^{III} 55.6 ml, W^{IV} 37.1 ml, W^{V} 18.5 ml).

(ii) 234.2 mg WO_3 ($\equiv$ 185.7 mg W) $\equiv$ 41.0 ml $0.01M$ $KMnO_4$
(Calc. for W^{III} 60.6 ml, W^{IV} 40.4 ml, W^{V} 20.2 ml).

Thus the tungsten in these solutions also appeared to be essentially in the tetravalent state.

Solutions of W^{IV} are moderately stable in air for 1–2 days, but after that time "tungsten blue" is deposited. Tetravalent tungsten appeared to be a moderately strong reducing agent, as it reduced ferric iron and cupric copper to a lower valency and gave "blue oxides" with Mo^{VI} (MoO_4^{-2} acidified with HCl) or W^{VI}.

Tungsten pentabromide was reduced in ethanolic medium by Zn and HBr. A brown solution was obtained, which appeared to be analogous to the tetravalent chloride solution but was less stable in air than the latter. Ethanolic HBr was used for the reduction, as the concentrated aqueous acid caused immediate hydrolysis to "tungsten blue". The tungsten pentabromide was prepared[6] by heating W metal powder (B.D.H.) to redness in a stream of bromine vapour carried by dry CO_2, and re-subliming the brownish-violet sublimate in dry CO_2. Analyses for W and Br were carried out in a manner analogous to that described for WCl_6. Found: W 31.6, Br 68.1. (Calc. for WBr_5: W 31.5, Br 68.5).

The existence of a W^{IV} complex with 8-hydroxyquinoline was investigated. When a strong solution of the acetone precipitate in HCl or some of the concentrated tungsten eluate was diluted with ethanol and added to an excess of ethanolic oxine (in a CO_2 atmosphere) a brown solid was precipitated. This was flocculated by the addition of

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* The dish was supported on glass rods in the desiccator, and not on zinc gauze because of the presence of HCl fumes in the vessel.

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ether, filtered off and washed with ethanol, ether and dried. Analyses for W, Cl and N showed that the composition of the powder varied. The latter was also insoluble in chloroform, and was resolved by acetone and water, or hydrochloric acid into soluble and insoluble fractions. Chemical tests suggested that the solid was W^{IV} basic chloride containing some mixed or loosely combined oxine hydrochloride and variable amounts of "tungsten blue".

SUMMARY

The reduction of WCl_6 in ethanol–acid medium by various metals was studied. Zinc dust gave complete reduction to the tetravalent state from which Zn or Zn + Fe could be removed by cellulose column chromatography or acetone-precipitation of W^{IV} respectively. Attempts to prepare a W^{IV}-oxine complex were unsuccessful.

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Received February 17th, 1958

DETERMINATION OF URANIUM IN URANIUM HEXAFLUORIDE MATERIAL*

by

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With the handling and processing of uranium hexafluoride, a method is needed to determine the uranium in the uranium hexafluoride material which contains volatile impurities, such as hydrogen fluoride and fluorocarbons. Hurd, *et al.*[1] developed a precise "knockout" method in which several hundred grams of uranium hexafluoride was transferred to a tared nickel cylinder, weighed, frozen, knocked out into a tared fluorothene beaker, and hydrolyzed by adding ice-cold water. The beaker and contents were then weighed. Aliquots of this uranyl fluoride solution were weighed, converted to the nitrate, ignited to urano-uranic oxide, and again weighed. The total uranium in the uranyl fluoride solution was calculated from the weight of the oxide, aliquot, and solution and was divided by the weight of the hexafluoride sample to obtain the percentage of uranium. While the precision of this method was satisfactory, large quantities of uranium hexafluoride were required, and two analysts were needed to perform the knockout operation. Also representative aliquots of the uranyl fluoride solution could not be obtained when fluorocarbons were present.

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* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

Olszewski[2] suggested a distillation step for the removal of fluorocarbons from the fluoride solutions which improved the precision and accuracy of the knockout method. Another modification by Cline and Lafferty[3] was the use of superheated steam (pyrohydrolysis) to convert the uranyl fluoride to urano-uranic oxide.

The major problem in the analysis of uranium hexafluoride material containing no non-volatile impurities is to weigh and hydrolyze a known amount of sample while keeping it free of metallic impurities. A fluorothene tube equipped with a flare nut, plug, and Teflon gasket (Fig. 1) was found to be a suitable container for weighing and handling the uranium hexafluoride which is transferred in a vacuum system (Fig. 2).

PROCEDURE

The cylinder of uranium hexafluoride to be sampled is placed in a hot water bath to liquefy the uranium hexafluoride, and then connected to the sampling system (Fig. 2). The weighed fluorothene tube is also connected to the sampling system by a flare fitting and evacuated; then approximately 7 g of the liquefied uranium hexafluoride is drained into it. The tube and hexafluoride are frozen with

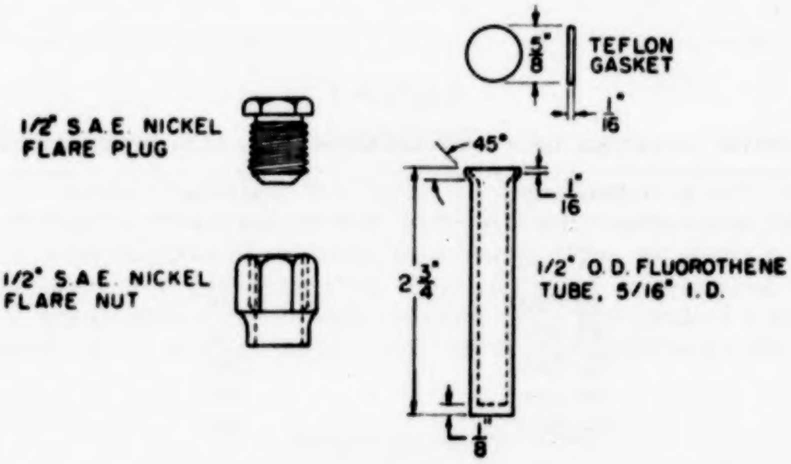
5"/8
TEFLON GASKET
1"/16
1/2" S.A.E. NICKEL FLARE PLUG
45°
1"/16
1/2" S.A.E. NICKEL FLARE NUT
2 3"/4
1/2" O.D. FLUOROTHENE TUBE, 5/16" I.D.
1"/8

Fig. 1. Fluorothene sample tube.

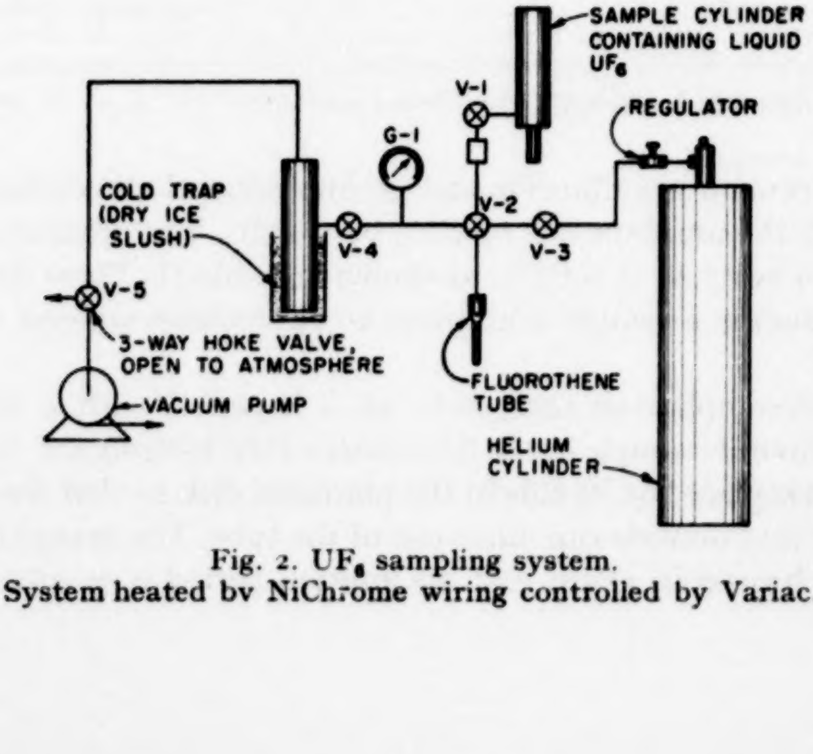
SAMPLE CYLINDER CONTAINING LIQUID UF6
V-1
REGULATOR
G-1
COLD TRAP (DRY ICE SLUSH)
V-2
V-4
V-3
V-5
3-WAY HOKE VALVE, OPEN TO ATMOSPHERE
VACUUM PUMP
FLUOROTHENE TUBE
HELIUM CYLINDER

Fig. 2. UF$_6$ sampling system.
System heated by NiChrome wiring controlled by Variac.

liquid nitrogen, and helium is let into the system to a pressure of one atmosphere. The tube is removed from the system, capped, dried in a desiccator for one h, and weighed. The tube is again frozen in liquid nitrogen, uncapped, and placed on its side in a weighed 200-ml platinum dish containing approximately 150 ml of ice-cold water. Small bubbles of air in the tube are removed by raising the open end of the tube slightly. When the hydrolysis of the uranium hexafluoride is completed, the tube is removed and rinsed, and the solution is evaporated to dryness under infrared heat lamps. The uranyl fluoride is pyrohydrolyzed at 850° and the oxide weighed. The oxide is analyzed spectrographically for metallic impurities and the weight is corrected for the amount found. From the weight of sample and oxide, the percentage of uranium in the uranium hexafluoride is calculated.

RESULTS

For control purposes, a large quantity of uranium hexafluoride was distilled to remove non-volatile material, liquefied, and a portion of the vapors exhausted at intervals into a vacuum system until the impurities remaining in the uranium hexafluoride were less than 0.01 wt.% hydrogen fluoride as shown by the freezing point depression method[4].

Samples of this pure uranium hexafluoride were processed according to the described procedure. The uranium in these control samples was determined to be 67.621 ± 0.007%, which is not significantly different from the theoretical value. The precision of a single analysis at the 95% confidence interval was ± 0.06% of the value, as shown in Table I.

TABLE I

URANIUM ANALYSIS OF PURE URANIUM HEXAFLUORIDE CONTROLS

Sample no.	*Uranium %*	*Sample no.*	*Uranium %*
1	67.583	7	67.629
2	67.624	8	67.633
3	67.610	9	67.628
4	67.631	10	67.634
5	67.642	11	67.620
6	67.635	12	67.587

Mean	67.621 ± 0.012*
Theoretical	67.620
Percent bias	0.001 ± 0.018
Precision of a single analysis	± 0.041 (± 0.06% of the value)

* The precision is expressed as the 95% confidence interval.

A mixture of uranium hexafluoride and perfluorodimethylcyclohexane (C_8F_{16}) was prepared in which the uranium was 67.26% by weight. The uranium in this mixture was determined to be 67.26 ± 0.03%, as shown in Table II. These data indicate that the per cent uranium in a sample containing an appreciable amount of fluorocarbons will be unbiased.

One analyst can complete an analysis in an 8 h period with a labor cost of 0.7 man-h. The hexafluoride sample in the fluorothene tube hydrolyzed in approximately 1 h, when the tube is placed on its side in the platinum dish so that the air bubbles can escape and the uranyl fluoride can move out of the tube. The uranyl fluoride solution is evaporated to dryness in $4^1/_2$ h and the ignition period is 30 min.

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Low uranium results were obtained when helium was not used to fill the void spaces around the hexafluoride in the tube before disconnecting it from the vacuum system. If air or nitrogen were permitted to fill these void spaces, a correction would have to be made for the extra weight of air or nitrogen trapped in the tube since it is capped near liquid nitrogen temperature. When the tube warms to room temperature, the weight of helium is slightly less than that of air which would occupy the same space but this difference in weight is less than 0.01% of the uranium.

TABLE II

URANIUM DETERMINED IN URANIUM HEXAFLUORIDE–PERFLUORODIMETHYLCYCLOHEXANE MIXTURE

Sample no.	*Uranium %*
1	67.23
2	67.27
3	67.26
4	67.25
5	67.28
6	67.26
Average	67.26 ± 0.03
Mixed by weight	67.26

SUMMARY

A rapid and precise method has been developed for the determination of uranium in uranium hexafluoride material that contains essentially no non-volatile impurities. Approximately 7 g of uranium hexafluoride is transferred into a tared fluorothene tube, weighed, frozen, and hydrolyzed in 150 ml of ice-cold water in a platinum dish. The solution is evaporated to dryness, and the residue is ignited to urano-uranic oxide and weighed. The precision of a single analysis at the 95% confidence interval is ± 0.06% of the value, with no significant bias.

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Received January 25th, 1958

THE SOLUBILITY AND THERMAL DECOMPOSITION OF SOME AMINE TETRAPHENYLBORON COMPOUNDS

by

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INTRODUCTION

The preparation of lithium tetraphenylboron was first reported by WITTIG *et al.*[1] Shortly afterward, he reported that, whereas the lithium and sodium salts of tetraphenylboron are water soluble, the potasssium, rubidium, cesium and ammonium salts are very insoluble[2]. Upon this basis, a method for the gravimetric determination of potassium was proposed. The reaction of tetraphenylboron with potassium has since been thoroughly studied and many publications have appeared concerning the optimum conditions for precipitation[3], the drying and decomposition ranges of the precipitate[4], its solubility[5-7], and the various types of analytical measurements that may be made[3].

While the potassium compound has received considerable attention, little has been reported on the ammonium and substituted ammonium compounds. The importance of an investigation of these compounds is shown by reports that sodium tetraphenylboron has been used to precipitate choline, histamine, certain alkaloids, and nitrogen containing pharmaceuticals[3]. It has also been suggested that identification of nitrogen containing compounds may be accomplished by characterization of tetraphenylboron precipitates[8]. A thermal investigation of these compounds would yield data as to drying temperatures, effect of amine structure on thermal stability, decomposition reactions, and decomposition products. Solubility data would also be of interest.

Present information regarding the thermal stability of the tetraphenylboron compounds is limited to the work of WENDLANDT[4,9]. These studies included the alkali, ammonium, mercury and silver tetraphenylborons. It was reported that the alkali metals were quantitatively converted to the corresponding metaborate and that the ammonium salt was transformed to boron oxide by heating in air. The transformation of the ammonium compound was not quantitative, however, due presumably to sublimation of the initial compound prior to the attainment of its decomposition temperature. The phenyl groups of the tetraphenylboron molecule were presumably oxidized to carbon dioxide and water. A differential thermal analysis study was not carried out.

Available solubility data are limited to potassium, rubidium, cesium, thallium, and ammonium tetraphenylboron[5-7,10]. Corresponding information on the substituted amine compounds is completely lacking. Solubility data and the variations in solubility with substitution would serve as a useful guide in predicting the behavior of other amine tetraphenylborons.

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EXPERIMENTAL PART

Reagents used

Sodium tetraphenylboron was obtained from the J. T. Baker Chemical Co., and was used without further purification. Eastman White Label amine hydrochlorides were the source of aliphatic amines. Pyridine was also an Eastman White Label product and the 2,2'-bipyridine was obtained from the G. Frederick Smith Chemical Co. The pyridine and 2,2'-bipyridine were purified by recrystallization of the perchlorate salts. These salts were formed by the slow addition of perchloric acid to an ethanolic solution of the amine. The resulting solid was filtered and recrystallized from a water–ethanol mixture. Acetonitrile, obtained from the Matheson, Coleman and Bell Division of the Matheson Co., was purified by the method of WAWZONEK AND RUNNER[11]. Spectro-grade cyclohexane was used as received from Distillation Products Industries. Commercial grade acetone was used for recrystallization. All other chemicals were reagent grade quality. Deionized water was used for all aqueous solutions.

Preparation and analysis of tetraphenylboron compounds

The amine tetraphenylboron compounds were prepared by the addition of a 5% excess of freshly prepared sodium tetraphenylboron solution to a $1 \cdot 10^{-2}M$ solution of the desired amine hydrochloride or perchlorate. The resultant precipitate was allowed to stand for 5 min and was then filtered, and washed several times with water. All amine compounds, with the exception of methylammonium tetraphenylboron, were recrystallized from an acetone–water solution. Methylammonium tetraphenylboron was used as precipitated.

All compounds were analyzed by titrimetric and absorptiometric measurements. In the titrimetric method, standard perchloric acid in glacial acetic acid was used to titrate the tetraphenylboron salt in anhydrous acetone to the crystal violet end-point[12]. Absorption maxima at 266 mμ and 274 mμ, characteristic of the tetraphenylboron ion[7], were used for measurement of the tetraphenylboron concentration in acetonitrile solutions of the aliphatic amine compounds. For the heterocyclic amine compounds, the measured absorbance included the absorbance of the protonated amine.

Absorptiometric measurements

Absorption spectra of solutions were obtained with a Cary Model 11 recording spectrophotometer, using 1- or 5-cm matched silica cells as required. All measurements were made at room temperature of approximately 25°.

Solubility measurements

Solubilities of the amine tetraphenylboron compounds were obtained by absorptiometric measurement of the tetraphenylboron content of aqueous solutions after equilibration of solid and solution at 25°. Moist, freshly precipitated compound was carefully washed with water and then placed in water in each of two flasks. One flask was maintained at 25° with constant agitation, while the other was held at 40–50° for one-half hour and then cooled to 25° with constant agitation. Samples were removed from each flask at regular time intervals until equilibrium was obtained. These heterogeneous samples were immediately filtered through a fine porosity glass filter, quantitative dilutions made if necessary, and the filtrate measured absorptiometrically.

Differential thermal analysis and thermal gravimetric analysis

The equipment used was the simultaneous automatic recording apparatus described by OSTROFF, EYRING AND SANDERSON[13]. All runs were made from room temperature to 1000° on samples of approximately 30 mg in an atmosphere of dry air flowing at a rate of 400 ml/min. The air was dried by passage through a 4 × 70 cm column packed with barium oxide. The heating rate for all samples was maintained constant at 8–10°/min.

The curves of Fig. 1 were plotted from decomposition data obtained as described above. The calculation of apparent molecular weight was made by assuming that the number of moles of compound remained constant through the decomposition reaction. Differential thermal analysis curves are plotted as scale deflection *vs.* temperature. As drawn, an exothermic reaction is indicated by an upward deflection in the differential thermal analysis curve.

Sublimation studies

Sublimation studies were carried out on two tetraphenylboron compounds. Evacuated sealed tubes containing samples of ammonium and pyridinium tetraphenylboron were prepared and partially immersed in an oil bath. As the bath was slowly heated, the tubes were observed for evidence of sublimation of the compounds.

RESULTS AND DISCUSSION

It was found that amine tetraphenylboron compounds can be easily prepared by the method described above. Most of the compounds were isolated in the pure state either from the reaction mixture or upon recrystallization of the crude precipitate from an aqueous acetone medium. The notable exception to this method of preparation and purification was the methylammonium compound. The unrecrystallized product had a m.p. of 209° and a tetraphenylboron content of 90.0%. Product recrystallized from an acetone-water mixture melted at 163-7° and had a tetraphenylboron content of 79.6% by titrimetric analysis. Methylammonium tetraphenylboron has a m.p.[8] 209-211° and 90.9% tetraphenylboron. It is apparent that a molecule of acetone becomes attached to the compound upon recrystallization.

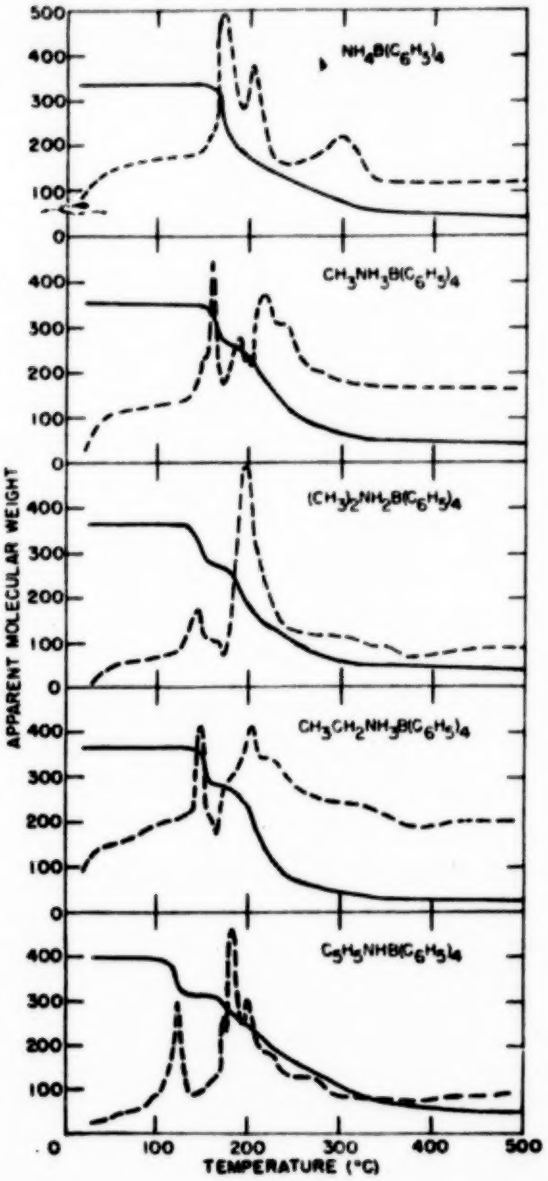

Fig. 1. Thermal gravimetric and differential thermal analysis curves for the decomposition of amine tetraphenylborons in air.

The titrimetic method for the analysis of potassium tetraphenylboron developed by FLASCHKA[12] was successfully adapted to the analysis of amine tetraphenylboron compounds. Titrimetic results on all compounds listed in Table I agreed to within *ca.* 2% of the theoretical percentage of tetraphenylboron. The composition of each compound

TABLE I

MINIMUM DECOMPOSITION TEMPERATURES AND SOLUBILITIES (25°) OF AMINE TETRAPHENYLBORONS

Tetraphenylboron compound	*Minimum decomposition temperature*	*Solubility* $(M \cdot 10^{-4})$
Ammonium	130°	2.88
Methylammonium	121°	36.3
Dimethylammonium	96°	16.3
Trimethylammonium	137°	3.87
Tetramethylammonium	312°	0.43
Ethylammonium	128°	28.3
Propylammonium	115°	9.03
Butylammonium	102°	11.2
Pyridinium	94°	1.99
2,2′-Bipyridinium	110°	—

was readily ascertained from these data. Spectrophotometric measurements confirmed these results.

Ultraviolet absorption spectra of the aliphatic amine tetraphenylboron compounds in acetonitrile were identical to spectra of the alkali metal compounds. Spectra of the heterocyclic amine compounds represented the summation of the protonated amine and tetraphenylboron. It is apparent that the tetraphenylboron ion is a much weaker base in acetonitrile than the amines investigated. However, it is sufficiently basic in acetone to be titrated with perchloric acid.

The amine tetraphenylborons were found to be soluble in acetone and in the alcohols, but insoluble in water. Solubilities in water at 25° are presented in Table I. It can be seen that solubility decreases with increasing chain length for mono-substituted amine compounds. In the methyl amines, solubility decreases with increasing methyl substitution. The unsubstituted ammonium compound falls between the trimethyl- and tetramethyl-ammonium compounds.

Minimum decomposition temperatures presented in Table I are the lowest temperatures at which a loss of weight in a thermal gravimetric analysis can be detected. The values given are considerably lower than melting points previously reported[8]. This apparent discrepancy is due to the fact that the initial decomposition in a thermal gravimetric analysis is not necessarily observed in a melting point determination.

With the exception of tetramethylammonium tetraphenylboron, the observed decomposition temperatures of the compounds investigated range between 95–137°. There is a definite dependency of the temperature upon the structure of the amine among the methyl substituted compounds. The order of decomposition temperature is: $NH_4 > CH_3NH_3 > (CH_3)_2NH_2 < (CH_3)_3NH \ll (CH_3)_4N$. This follows the same order as the base strength of the amines, in a reverse manner. In a mono-substituted aliphatic amine series, there is a general tendency toward lower temperatures with increasing chain length of the substituent group. It is evident that most amine tetraphenylborons should be dried at temperatures below 100°.

Upon heating in air, tetraphenylboron compounds undergo reactions which ultimately result in the formation of boron oxide. The oxide formation appears to be a gradual process over the temperature range of 300–1000° due to the slow combustion

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of tars and residues. The thermal decomposition curves of Fig. 1 show a gradual slope with a final weight below the theoretical value for boron oxide. Similar results observed with other tetraphenylboron compounds were considered to be due to loss of boron by sublimation of the initial compound[4]. Sublimation was not observed in the present investigation in studies at reduced pressure nor by endothermic reactions in differential thermal analyses. An endothermic sublimation of the initial compound or of an intermediate decomposition product, proceeding simultaneously with a decomposition reaction, is not precluded since it could be masked by the exothermic decomposition reaction. Thus, it is possible that boron is lost through sublimation of an intermediate compound since loss of the final product is not a feasible consideration due to the extremely low vapor pressure of boron oxide below 1000°[14].

The loss of boron described above complicates the interpretation of thermal data. However, the following sequence of decomposition reactions is postulated.

$$R_3NHB(C_6H_5)_4 \rightarrow R_3NB(C_6H_5)_3 + C_6H_6 \quad \ldots\ldots\ldots \tag{1}$$

$$2R_3NB(C_6H_5)_3 \xrightarrow{[O]} 2R_3NC_6H_5BOC_6H_5 + C_{12}H_{10} \quad \ldots\ldots\ldots \tag{2}$$

$$2R_3NC_6H_5BOC_6H_5 + 2R_3NB(C_6H_5)_3 \rightarrow 2R_3NB_2O(C_6H_5)_4 + C_{12}H_{10} + 2R_3N \tag{3}$$

$$R_3NB_2O(C_6H_5)_4 \rightarrow B_2O(C_6H_5)_4 + R_3N \quad \ldots\ldots\ldots \tag{4}$$

$$B_2O(C_6H_5)_4 \xrightarrow{[O]} B_2O_2(C_6H_5)_2 \xrightarrow{[O]} B_2O_3 + 2C_{12}H_{10} \quad \ldots\ldots \tag{5}$$

The initial decomposition (eqn. 1) involves the loss of a phenyl group as indicated by the consistent loss in molecular weight for all compounds studied (Fig. 1). Benzene, biphenyl and phenol (formed in side reactions) are definitely indicated in the absorption spectrum of the effluent gas mixture. Boron containing intermediates, $R_3NB(C_6H_5)_3$, $R_3NC_6H_5BOC_6H_5$ (phenyl diphenylboronite), $B_2O(C_6H_5)_4$ (bis-diphenylboron oxide), and $B_2O_2(C_6H_5)_2$ (bis-phenylboron dioxide) can be identified from the thermal curves and are known intermediates in the oxidation to boric oxide[15,16]. The role of the amine in stabilizing these intermediates through coordination is a significant feature of the decomposition process. The resultant thermal stability of the amine borates can be utilized in the determination of amines with sodium tetraphenylboron.

ACKNOWLEDGEMENTS

The authors wish to thank E. I. du Pont de Nemours and Co. for the research grant which made this work possible. Our thanks are also extended to DR. LEROY EYRING for his help in the collection and interpretation of the thermal data.

SUMMARY

Differential thermal analysis, thermal gravimetric analysis and solubility studies were carried out on 10 amine compounds of tetraphenylboron. Aliphatic amines of C_1 through C_4, as well as pyridine and 2,2'-bipyridine, were considered. Both solubility and thermal decomposition temperature were shown to vary over a wide range. This variation may be related to the substitution in the amine. Upon heating, all compounds were transformed into boron oxide by a complex series of reactions.

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Received February 4th, 1958

THE ANALYSIS OF VOLATILE LIQUID MIXTURES BY THERMAL CONDUCTIVITY MEASUREMENTS ON THEIR VAPORS

by

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INTRODUCTION

The purpose of the present study was to determine the reliability with which one might determine the compositions of a variety of binary mixtures of liquids by measurements of the thermal conductivity of their vapors. One could approach the problem by completely volatilizing a small sample, or by using a large volume of liquid and vaporizing small portions as was done in this study. Obviously, the method could also be extended to more complex mixtures in which changes in composition were due primarily to differences in one component.

An absolute measurement of thermal conductivity was desired in order to determine how closely the experimental values could be predicted using the recently published equation of Lindsay and Bromley[1]. In order to do this, sensitivity was sacrificed which, however, could be regained in an intended application by using a differential method together with empirical calibrations[2,3,4]. A Wheatstone bridge

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[b] Taken from a thesis submitted by Harry W. Linde in partial fulfillment of the requirements for a Ph.D. degree in September, 1953.

consisting of three precision resistors and one thermistor was employed. Using a thermistor, one could easily obtain suitable sensitivity while working at a low detector temperature, thereby minimizing the chance of thermal decomposition of the organic vapors. The bridge was balanced by adjusting the current so as to restore the thermistor to its original resistance. In this way, changes in thermal conductivity as well as possible changes in convection, due to differences in the temperature of the thermistor, were minimized. The relationship between current and thermal conductivity may be expressed:

$$I^2 = \frac{k(t_1 - t_2)J \cdot S}{2R} \qquad (1)$$

where: I = current flowing to bridge, in amperes
k = thermal conductivity, in cal/cm sec °C
J = the mechanical equivalent of heat
R = thermistor resistance, in ohms
S = "shape factor" which takes into account the shape of the cell, heat lost through the supporting wires, etc.
t_1 = temperature of the thermistor
t_2 = temperature of the wall

For a given cell with constant thermistor and wall temperatures, equation (1) reduces to:

$$I^2 = (\text{a constant}) \times k$$

A variety of systems were studied: acetone-water; acetone-methanol; acetone-ethanol; acetone-diethyl ether; acetone-carbon disulfide, acetone-carbon tetrachloride, acetone-chloroform, ethanol-methanol and methanol-benzene. Only two typical systems will be presented here for purposes of illustration. Likewise, although measurements were made at four thermistor temperatures, data will be given only for one.

EXPERIMENTAL

Reagents

The solvents used to make the binary mixtures were reagent grade and were used as received. The mixtures were made up by weight. The methane, ethylene and normal butane were Phillips Petroleum Company Research grade with purities of 99.9 to 100.0 mole %. Gaseous ethyl chloride was obtained by allowing Eastman White Label ethyl chloride to boil and the vapor to flow through the system.

The nitrogen was Airco's prepurified grade and was passed over anhydrous magnesium perchlorate before use. The argon was Airco's lamp grade, and the carbon dioxide was the ordinary commercial grade.

Apparatus

One thermistor in a Veco Model 139-2 thermal conductivity cell (Victory Engineering Corporation, Union, New Jersey) was used as a detector. The three remaining arms of the Wheatstone bridge were precision wire-wound resistors as shown in Fig. 1. The bridge was balanced by adjusting R_5. At a resistance of 750 ohms, the temperature of the thermistor was 57°. The cell block was placed in an oil-bath thermostat maintained at 30.00 ± 0.02°. Using a Rubicon potentiometer sensitive to 0.1 mV, the minimum detectable change in conductivity was $0.4 \cdot 10^{-7}$ cal/cm sec °C.

The cell block, flowmeters, vaporizers and gas cylinders were connected into a gas train using 8-mm glass tubing and glass-to-glass connections held together by Tygon tubing. The gas flowed from a cylinder to the bridge through a Fischer and Porter rotameter calibrated from 0 to 690 ml/min. The volume of this gas train was about 40 ml between the flowmeter and the cell, excluding the vaporizer tubes. The vaporizers were glass test tubes 18 × 250 mm deep into which fritted glass dispersion tubes were dipped. Two tubes were connected in series, and both were held in a water bath controlled at 25 ± 0.1°. A thermometer, graduated in 0.1° inserted in the test liquid was never observed to fall below the temperature of the bath during the vaporization. Vaporization was conducted by passing nitrogen at a rate of 20 to 100 ml/min through a depth of 6 cm of liquid in each tube. In most cases, the reading obtained after 15 min remained constant and was readily reproducible on other occasions. However, a check of the stability was always made after another 30 min.

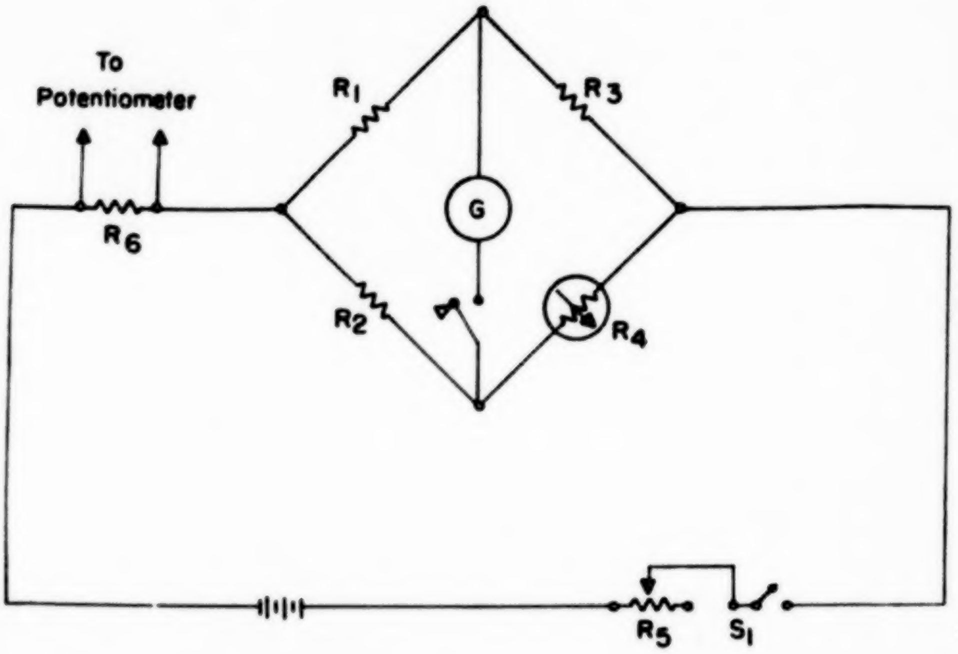

Fig. 1. Bridge circuit $R_1 = R_2 =$ 1500 ohms
$R_3 =$ 750 ohms
$R_4 =$ thermistor (resistance $= R_3$ at balance)
$R_5 =$ current adjuster, 1000 ohm "Helipot"
$R_6 =$ potential dropping resistor, 100 ohm
$S_1 =$ SPST on-off switch
(All of the resistors were precision, wire-wound and had tolerances of ± 1%)

Calibration

In order to calibrate the bridge in terms of thermal conductivity, *k*, a series of pure gases of known conductivities were allowed to flow through the gas train until a steady bridge current was attained (about 4 min). To be sure that a stable value had been reached, the flow was continued for another 10 min and the current again measured. In Table I, the squares of the observed bridge currents are compared with the thermal conductivities of the pure gases. The values of

TABLE I

STANDARD GASES FOR CALIBRATION

Gas	*Thermal conductivity*[2,3,4] $10^7 \cdot k_{50^\circ}$	*Bridge current squared* $10^{-6} \cdot A^2$	*Coeff. of variation* %	*Number of observations*
Methane	880	16.614	0.07	2
Nitrogen	650	13.418	0.06	6
Ethylene	528	11.717	0.05	2
Argon	448	10.189	0.11	6
n-Butane	428	10.362	0.03	2
Carbon dioxide	427	9.847	0.04	9
Ethyl chloride	307	8.066	0.06	3

thermal conductivity used here were calculated from data given by PALMER AND WEAVER[2], DAYNES[3] and WEAVER[4]. The coefficient of variation (standard deviation expressed as a percent of the mean) and the number of observations for each gas are also given in Table I. The standard deviation was calculated by the method of DEAN AND DIXON[5]. The data in Table I, when plotted, gave a linear calibration curve (Fig. 2), which was used to convert observed values of bridge current to thermal conductivity.

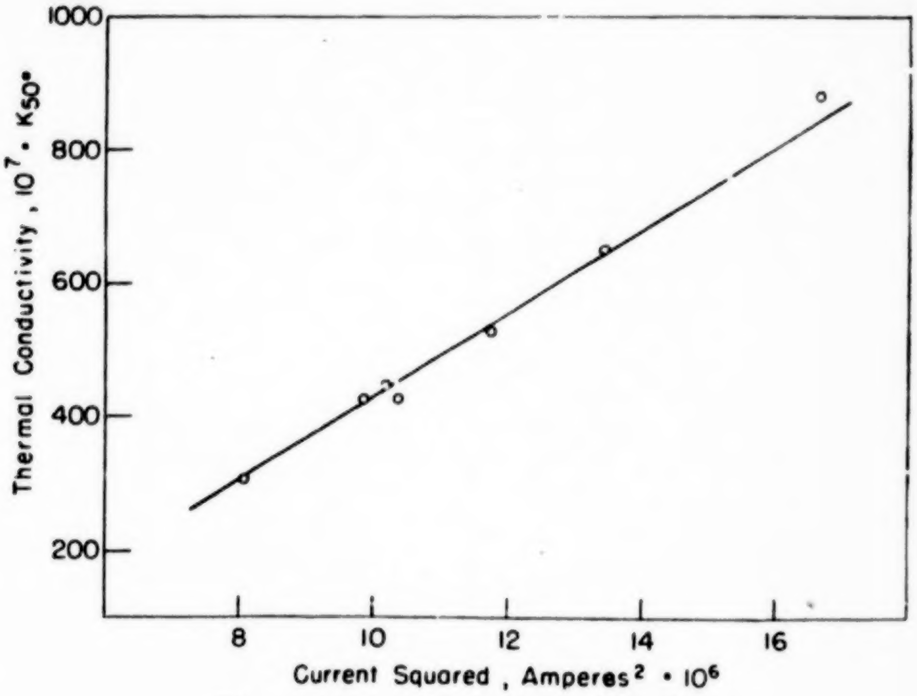

Fig. 2. Thermistor bridge calibration.

Evaluation of vaporization variables

The degree of saturation of the carrier gas was studied by connecting in series, eight vaporization tubes, measuring the thermal conductivity, removing one tube, remeasuring the conductivity, etc. For most liquids, no difference was noted in going from eight tubes to one. However, with highly volatile liquids such as diethyl ether and carbon disulfide, differences were produced by going from two tubes to one, so two tubes in series were always employed.

Liquid depths greater than 2 cm were found to give the same thermal conductivity providing the flow rate of the carrier gas was less than about 100 ml/min. A flow of 20 ml/min was usually employed.

Changes in the composition of the liquid due to vaporization losses were followed at 5-min intervals for 1 h or more. Generally, a steady value was reached in about 10 min which was checked for constancy over a period of at least 30 min. However, binary mixtures of acetone with carbon disulfide continually changed, particularly those samples having initial compositions of 80% or more of one component. Two "pure" liquids, acetone and chloroform also drifted. Acetone required 3 h to decrease to a stable value about 3.5% below the reading obtained after 15 min, indicating the presence of a better-conducting impurity. The decrease for chloroform was less severe, the constant value after 1 h being 1% below the 15-min value. In this case, the 0.75% ethanol, present as a preservative in the reagent, was undoubtedly the culprit.

RESULTS

The data in Table II indicate that the observed values for pure liquids were generally in line with the respective vapor pressures and thermal conductivities. Water was an exception, but it is known to form mixtures with nitrogen which exhibit a conductivity maximum[3].

The acetone-water system was chosen as a typical case to illustrate the precision of the data obtainable on binary mixtures as well as to show the closeness of agreement with values calculated from LINDSAY AND BROMLEY's equation[1]. Replicate

TABLE II

PURE LIQUIDS

Liquid	*Thermal conductivity*[2,3,4] $10^7 \cdot k_{50°}$	*Vapor pressure*[8] *25°, mm*	*Bridge current squared* $10^{-6} A^2$	*Coeff. of variation* %	*No. of observations*
Methanol	385	128	13.025	0.03	4
Ethanol	333	59	13.061	0.0	2
Chloroform	—	199	10.221	0.25	4
Carbon tetrachloride	154	115	13.257	0.27	2
Diethyl ether	353	537	10.498	0.01	4
Acetone	259	229	11.370	0.08	3
Carbon disulfide	—	365	9.036	0.08	3
Water	434	24	13.535	0.06	3

analyses were made on fresh aliquots of sample. Table III summarizes the experimental observations on various acetone–water mixtures; Fig. 3 presents the observed and the calculated data as well as the total vapor pressure for the system[6]. One can see that both the precision (about 0.1%) and the agreement with the calculated values (3% or less) were quite satisfactory. These figures for reproducibility were typical of the systems studied except acetone mixed with chloroform or carbon disulfide as mentioned earlier.

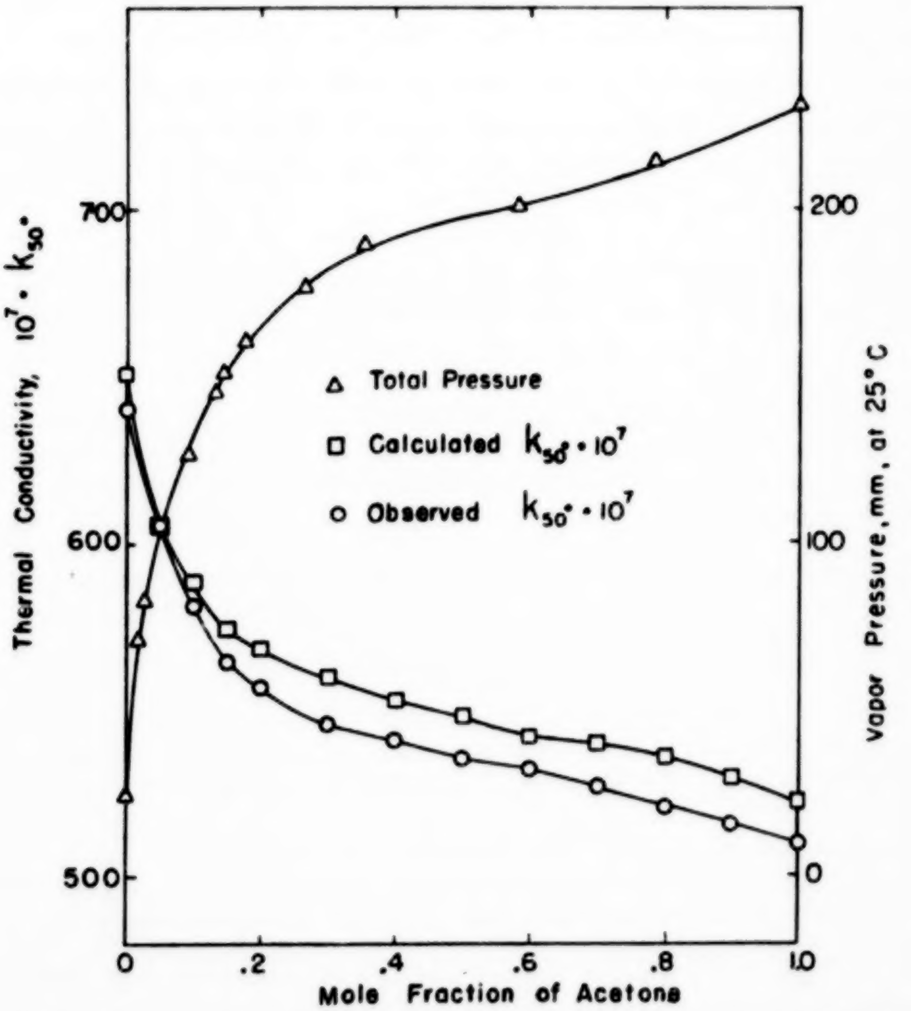

Fig. 3. Calculated and observed conductivities of the acetone–water–nitrogen system using vapor pressure data from reference 6.

TABLE III

ACETONE–WATER SYSTEM

Mol fraction acetone	*Thermal conductivity $10^7 \cdot k_{50°}$*	*Bridge current squared 10^{-6} A^2*	*Coeff. of variation %*	*No. of observations*
0.050	605	12.871	0.14	4
0.100	581	12.404	0.12	4
0.150	564	12.145	0.18	4
0.200	557	12.041	0.11	5
0.300	545	11.868	0.14	4
0.400	540	11.785	0.07	4
0.500	535	11.710	0.07	4
0.600	532	11.655	0.15	5
0.700	527	11.594	0.17	3
0.800	521	11.492	0.11	4
0.900	516	11.397	0.13	5

The acetone–carbon disulfide system (Fig. 4) is one in which the vapor pressure curve goes through a pronounced maximum while the conductivity goes through a smaller minimum. In practice, this ambiguity could be eliminated by making a se-

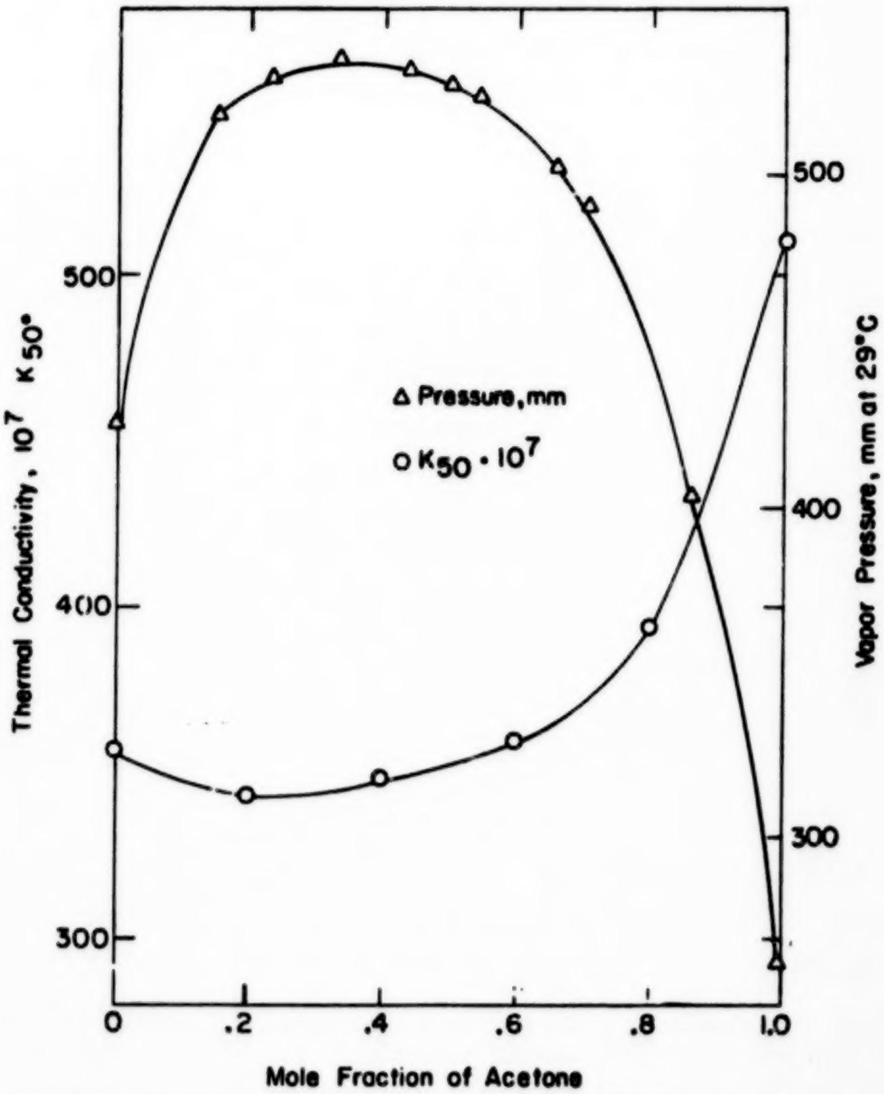

Fig. 4. Conductivity and pressure of acetone and carbon disulfide vapors in nitrogen using pressure from reference 7.

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cond conductivity measurement after adding a small amount of either component or by changing an experimental variable.

Among the other systems studied, acetone-ethanol and acetone-methanol were similar to one another and to acetone-water. They were without maxima or minima, and thus could be readily analyzed by this technique. The systems with minima in the conductivity *vs.* composition curve, acetone-ether, acetone-carbon tetrachloride, and benzene-methanol, as well as the one with a maximum, acetone-chloroform, would require an additional analysis as indicated in the previous paragraph, in order to arrive at a unique result for the composition. As might be expected from their chemical and physical similarities, ethanol, methanol and their mixtures can barely be distiguished from one another by this technique.

DISCUSSION

In principle, systems having a maximum or minimum could be analyzed by measuring the thermal conductivity at two temperatures. Unfortunately, the differences in the temperature coefficients of thermal conductivity are usually not very great. As a result, attempts to do this type of differentiation on the acetone-chloroform and benzene-methanol systems were far from satisfactory. A change in the temperature of the sample would probably have yielded better results but was dismissed as impractical.

As mentioned earlier, the apparatus used for this study left much to be desired from the standpoint of sensitivity. In practice an empirically calibrated, unbalanced-bridge circuit would undoubtedly be used, thereby affording much higher sensitivity. In that case, the technique might find application in the analysis of process streams or in following solvent removal in drying operations. The analysis of small volumes of liquid after complete volatilization of the sample is another interesting possibility.

ACKNOWLEDGEMENT

The authors wish to thank the Atomic Energy Commission for partial support of this study, and the Allied Chemical and Dye Corporation for generous fellowship support (to H.W.L.).

SUMMARY

The composition of solutions of volatile liquids can be determined by volatilization into a stream of inert gas and measurement of the thermal conductivity of the resulting gas mixture. The method is directly applicable to binary liquid mixtures which do not show maxima or minima in the conductivity–composition curve and, with modification, it may be applied to the analysis of other mixtures.

The observed and calculated thermal conductivities for the acetone-water-nitrogen system showed good agreement that was typical of a number of systems.

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Received January 25th, 1958

DETERMINATION OF ZINC IN PLANT MATERIALS USING ION-EXCHANGE CHROMATOGRAPHY*

by

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The most reliable method for the determination of zinc in plant materials has been the dithizone procedure[1]. That method usually requires three different separation and extraction steps to eliminate other ions which interfere in the zinc determination. These steps are not only time-consuming but may result in the loss of zinc or contamination of the solution by zinc and other interfering elements. It usually is possible to complete approximately 24 analyses in one day using the dithizone procedure. Another disadvantage to the dithizone method is the use of carbon tetrachloride to extract the zinc-dithizone complex. Where a large number of analyses are to be performed this organic extractant may create a health hazard due to its toxic fumes.

RUSH AND YOE[2] have described a new reagent for zinc, namely; Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene). They have recorded some of the essential analytical properties of the zinc-zincon complex, and have given a method for the determination of zinc. A large number of other elements interfere in the zinc determination. Many of these elements such as calcium, magnesium, manganese, iron, and copper commonly occur in plant materials.

The use of ion-exchange chromatography for the separation of certain elements is becoming more widespread. KRAUS AND MOORE[3] using the anion exchanger Dowex 1-X8 were successful in separating nickel, manganese, cobalt, copper, iron, and zinc. A similar technique has been described by JENTZSCH AND FROTSCHER[4].

A method[5] proposed for the determination of zinc in plant materials by the use of Zincon, after separation of interfering metals by ion-exchange, has given erratic results in this laboratory. This may be due to the interference of ammonium ion from the buffer**, incomplete replacement of the adsorbed zinc by the use of the prescribed volume of 0.005N hydrochloric acid, and the leakage of iron(III) into the zinc eluate.

The following proposed method eliminates the problems mentioned above and lends itself very satisfactorily for the routine and accurate determination of microgram quantities of zinc in the plant materials.

APPARATUS AND REAGENTS

All transmittancies and absorption spectra were performed on a Bausch and Lomb "Spectronic 20" spectrophotometer. A Beckman pH meter, Model N-1 was used for the pH measurements. Only Pyrex brand glassware was used throughout the procedure.

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* Arizona Agr. Expt. Sta. Tech. Paper No. 440.

** Unpublished data.

The ion-exchange columns were constructed as follows. A short piece of glass tubing (50 mm in length) was affixed to the bottom of a test tube having a length of 150 mm and an inside diameter of 13 mm. A short piece of plastic tubing and a clamp, or more preferably a glass stopcock was placed at the end of the glass tube. A small plug of glass wool was placed in the bottom of the test tube to prevent the exchange resin from moving through the tubing.

A slurry of Dowex 1-X8, 50–100 mesh was prepared using 1*N* sodium hydroxide. The column was filled approximately half with deionized water and the slurry was then introduced into the column. The liquid was permitted to flow from the column, thereby aiding the settling of the resin. At no time was the liquid permitted to fall below the surface of the resin. This procedure was continued until a column of resin 70 mm high was obtained. The resin contained small amounts of zinc as a contaminant and therefore was washed further with 100 ml of 1*N* sodium hydroxide. The column was then treated with 50 ml of 2*N* hydrochloric acid. The resin was then ready for use A series of eight columns were constructed, the flow rates ranging from 1–3 ml/min.

A CLARK AND LUBS buffer system of pH 9.0 was used[6]. A 10 p.p.m. standard solution of zinc was made using zinc metal dissolved in a small amount of concentrated hydrochloric acid. The Zincon reagent was prepared by dissolving 0.130 g of the reagent in 2 ml of 1*N* sodium hydroxide and diluting to 100 ml with deionized water. All other reagents and solutions were prepared using analytical or reagent grade chemicals. All water used was deionized by passage through a combined cation and anion exchange system.

SEPARATION AND ANALYTICAL PROCEDURE

Weigh a 1-g sample of plant material, containing less than 50 γ Zn, into a 50-ml beaker and place in a muffle furnace. Dry-ash the sample at a temperature of 475–500° for approximately 1 h. After the beaker has cooled, add 5 ml concentrated nitric acid, 5 ml water, and 2 ml 70–72% perchloric acid in the above order and place the beaker on a hotplate over medium heat for 1 h. Then raise the heat and permit the mixture to go to dryness. If unoxidized organic material remains after the beginning stages of the high heat treatment, remove the beaker from the hotplate, cool, and repeat the acid treatment.

To the oxidized plant ash add 10 ml 2*N* hydrochloric acid and bring the residue into solution. Filter the mixture through Whatman No. 40 paper and wash the filter with three 5-ml portions of 2*N* hydrochloric acid. A wooden filter rack may be attached above the ion-exchange columns with the filter stems placed inside the top of the ion-exchange tube. In this manner the filtrate goes directly into the column and not into a separate beaker, thereby possibly reducing loss or contamination through transference. If desirable, a beaker can be used to catch the filtrate. Introduce the filtrate, containing less than 50 γ Zn, into the ion-exchange column. Rinse the beaker with 2*N* hydrochloric acid. Permit the solution and rinsings to pass through the column (not below the upper level of the exchanger) and discard the eluate. Wash the column with 40 ml of 0.5*N* hydrochloric acid and discard these washings. Replace the adsorbed zinc on the column with 30 ml 1*N* sodium hydroxide, retaining this washing in a 50-ml beaker. To the beaker add 5 ml of buffer solution and adjust the solution to pH 9.0 with hydrochloric acid.

Transfer the contents of the beaker to a 50-ml volumetric flask; add 1 ml Zincon solution, dilute to the mark with water, and mix. Read the transmittancy or absorbance of the resultant colored solution within 20 min in a suitable spectrophotometer at 620 mμ. Compare the spectrophotometric readings with a working curve prepared by subjecting standard zinc solutions to the exchange procedure above or construct a standard curve for zinc standards not run through the exchanger and make the appropriate corrections for the exchanger blank. Each column after being used should be washed further with 30 ml 1*N* sodium hydroxide and 30 ml 2*N* hydrochloric acid before reusing.

It is recommended that the exchange resin be replaced after 6 separations have been accomplished. The low cost of the required amount of resin makes this replacement entirely practical. It is preferable to leave the columns filled with water when not being used. When the first increments of 2*N* hydrochloric acid are introduced into the columns containing the 1*N* sodium hydroxide, small air pockets are formed, probably because of heat of neutralization. These pockets are removed by further leaching until the prescribed amount of 2*N* hydrochloric acid is used.

EXPERIMENTAL

To further test the removal of interfering ions and the quantitative replacement of adsorbed zinc a number of experiments were conducted. Previously it was noted[2] that up to 500 γ of iron(III) may be removed by an ion-exchange technique. To further clarify this point synthetic solutions containing iron(III) and zinc were pre-

TABLE I

REMOVAL OF INTERFERING IONS BY ION EXCHANGE COLUMNS

Ion present (γ)		*Zn present (γ)*	*Zn found (γ)*
Fe^{+3}	200	30.0	29.7
Fe^{+3}	600	30.0	28.9
Fe^{+3}	800	30.0	22.0
Fe^{+3}	600	30.0	30.0[a]
Fe^{+3}	600	30.0	30.0[b]
Fe^{+3}	600	30.0	30.0[c]
Mn^{+4}	200	30.0	29.8
Mn^{+4}	800	30.0	30.4
Cu^{+2}	100	30.0	31.0
Cu^{+2}	50	30.0	30.5
Cu^{+2}	30	30.0	31.0
Cu^{+2}	30	20.0	19.6
Cu^{+2}	30	10.0	11.0

[a] 20 ml 1% sodium sulfite added prior to transference to column.
[b] 15 ml 5% hydroxylamine hydrochloride added prior to transference to column.
[c] 15 ml 1% sodium arsenite added prior to transference to column.

pared and analyzed in the manner described above. As shown in Table I, amounts of iron in excess of 600 γ interfere in the subsequent determination of zinc as all the iron is not replaced by 0.5N hydrochloric acid but appears in the 1N sodium hydroxide eluate. Small amounts of iron seriously affect the development and/or stability of the zinc-zincon complex.

The addition of certain reducing agents may increase the upper limit of iron that can be tolerated (Table I). The difference in adsorption and replacement of the chloro-complexes of iron(II) and iron(III) are large enough[4] that a conversion to the iron(II) state might aid the separation of iron from zinc. Other methods to increase the amount of iron separated from zinc include decreasing the particle size of the resin and/or decreasing the flow rate of the columns*. Since the proposed method recommends using a 1-g plant sample, it is doubtful that quantities of iron in the interfering range will be found.

RESULTS

The quantitative recovery of zinc from the exchange column is satisfactory (Table II) and as shown in Table III, the accuracy of the proposed method compares favorably with the official A.O.A.C. method[1]. The proposed procedure is more rapid than the dithizone method.

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* Unpublished data.

TABLE II

RECOVERY OF ZINC FROM ION EXCHANGE COLUMNS

Zinc present (γ)	*Zinc found (γ)*	*Zinc present (γ)*	*Zinc found (γ)*
10.0	10.0	30.0	29.7
10.0	10.2	40.0	38.2
20.0	20.2	40.0	37.4
20.0	19.4	50.0	47.0
30.0	30.5	50.0	48.5

TABLE III

COMPARISON OF THE PROPOSED METHOD AND THE A.O.A.C. METHOD FOR THE DETERMINATION OF ZINC IN PLANT MATERIALS

Sample	*Proposed method (p.p.m. Zn)*	*A.O.A.C. method (p.p.m. Zn)*
Peach leaves	15.2	15.0
Peach leaves	14.3	15.3
Pecan leaves	21.5	22.8
Grapefruit leaves	12.9	13.8
Grape leaves	44.4	44.1
Lettuce leaves	27.0	29.4
Cantaloupe stems	40.2	40.0

To further test the reliability of the proposed method, a recovery investigation was conducted. Known amounts of zinc were added to particular plant samples whose zinc concentration was determined previously by the proposed method. These samples were ashed and analyzed as described in the above procedure. The recovery values are shown in Table IV.

As a further check on the proposed method, a synthetic ash solution was prepared containing many of the elements found in plant materials. Known amounts of zinc were added to 10-ml portions of the ash solution and analyzed as described. The results are shown in Table V.

DISCUSSION

The use of 1*N* sodium hydroxide was satisfactory for replacing the exchanger-adsorbed zinc. This eliminates the need for a controlled normality of hydrochloric acid to replace the zinc. The adsorption of cadmium- and lead-chloro complexes on an anion exchanger has been noted[4]. The normality of hydrochloric acid required to replace the cadmium and lead was found to be less than that required for zinc and therefore the cadmium and lead may appear in the sodium hydroxide fraction. KALLMAN *et al.*[7] observed that by using a mixture of sodium hydroxide and sodium chloride they were able to replace zinc and lead from Dowex 1-X8 but cadmium remained on the column.

TABLE IV

RECOVERY OF ZINC ADDED TO SELECTED PLANT SAMPLES

Sample	*Zn added* *(γ)*	*Zn found* *(γ)*	*Recovery* *(γ)*
1	0.0	21.5	
	20.0	42.5	21.0
2	0.0	21.0	
	10.0	29.7	8.7
3	0.0	25.0	
	10.0	34.6	9.6
4	0.0	15.0	
	20.0	34.6	19.6
5	0.0	10.0	
	30.0	37.0	26.9
6	0.0	37.0	
	10.0	45.6	8.6
7	0.0	15.0	
	10.0	25.7	10.7

TABLE V

DETERMINATION OF ZINC IN SYNTHETIC ASH SOLUTION

	Zinc present *(γ)*	*Zinc found* *(γ)*
10 ml ash solution[a]	10.0	9.3
10 ml ash solution	30.0	30.1
10 ml ash solution	40.0	37.4
10 ml ash solution	50.0	47.0

[a] 10 ml of ash solution contains the following:

30 mg K^+	6 mg PO_4^{-3}	0.1 mg Mn^{+4}
60 mg Ca^{+2}	2.5 mg Ni^{+2}	0.1 mg Al^{+3}
20 mg Mg^{+2}	0.5 mg Fe^{+3}	0.025 mg Co^{+2}
10 mg Na^+		0.005 mg Mo^{+6}

It is extremely unlikely that any appreciable amounts of lead and cadmium would be found in plant tissue. KEATON[8] found no lead in the tops and roots of barley growing on a soil which did not receive applications of lead. However, it appeared advisable to study the influence of lead on the development of the zinc–zincon complex. In amounts up to 100 γ, lead did not interfere in the determination of zinc with zincon.

JACKSON AND BROWN[5] used 1 N hydrochloric acid to remove interfering ions from Dowex 1-X8 prior to the removal of zinc. However, KRAUS AND MOORE[3] used 0.5 N hydrochloric acid to remove iron(III). Results in this laboratory show that 0.5 N hydrochloric acid was superior to 1 N hydrochloric acid in removing relatively large amounts of interfering elements, particularly iron(III).

The proposed method is accurate and rapid for the determination of zinc in plant materials. For the routine analysis of a large number of samples, the procedure could he made more rapid by possibly altering the strength and volume of the 1*N* sodium bydroxide solution so that the addition of 5 ml of the buffer would bring the solution to pH 9.0 without further adjustment.

ACKNOWLEDGEMENT

Thanks are due Mr. GLENN E. PRIELIPP of the Dow Chemical Company, Midland, Michigan, for supplying experimental samples of Dowex 1-X8 resin.

SUMMARY

The objective of this investigation was to develop a rapid and accurate method for the determination of zinc in plant materials. An ion-exchange separation technique to eliminate interferences in the Zincon procedure for zinc is described. Comparison with the A.O.A.C. method and evaluation of zinc recovery studies show the proposed method to be satisfactory for the analysis of microgram amounts of zinc in plant materials.

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Received February 25th, 1958

THE DETERMINATION OF FORMALDEHYDE AND ACETALDEHYDE LIBERATED IN THE PERIODATE AND NINHYDRIN REACTIONS

by

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Small quantities of formaldehyde and acetaldehyde may be determined colorimetrically by means of chromotropic acid[1,2] and *p*-hydroxybiphenyl[3-5] respectively. In the case of biological materials these have their greatest application to the determination of these aldehydes after their liberation by chemical reaction. Table I is a summary of the more generally used of these reactions.

TABLE I

Chemical reaction employed	*Substance or group determined*
Formaldehyde liberation	
1. action of concentrated sulphuric acid	glycolic acid[6]
2. action of ninhydrin at pH 5	glycine[7,8]
3. action of periodate in acid medium	$CH_2OH{\cdot}CO$-, $CH_2OH{\cdot}CHOH$-[9-11]
4. action of periodate in neutral medium	serine[9,12,13]
Acetaldehyde liberation	
1. action of concentrated sulphuric acid	lactic acid[13-16]
2. action of ninhydrin at pH 5	alanine[17-19]
3. action of periodate in acid medium	$CH_3{\cdot}CHOH{\cdot}CO$- and $CH_3{\cdot}CHOH{\cdot}CHOH$- [20,21]
4. action of periodate in neutral medium	threonine[22]

The individual reactions are specific for the group of substances concerned but when applied to biological materials, formaldehyde and acetaldehyde are usually liberated simultaneously and in particular, formaldehyde tends to interfere with the colorimetric determination of acetaldehyde. SHINN AND NICOLET[21] have achieved the separation of these aldehydes after reaction of mixtures of glycine and alanine with ninhydrin but the apparatus employed may not be generally applicable. COX[20] has described a simple aeration technique for the separation of the acetaldehyde liberated from pregnanetriol by reaction with periodate.

When reactions 2, 3, and 4 are applied to biological materials, it is preferable as an initial step to separate the liberated aldehydes from the reaction mixtures by distillation at 100°. The recovery of formaldehyde and acetaldehyde in microgram quantities by distillation at 100° has already been discussed[9,11]. The COX aeration technique has proved very successful in the separation of the formaldehyde and acetaldehyde present in these distillates. Formaldehyde and acetaldehyde show marked differences in properties with respect to aeration at room temperature (20°). When aqueous solutions containing both aldehydes in microgram quantities are aerated, acetaldehyde is completely removed and may be trapped in bisulphite solution whereas formaldehyde remains quantitatively in the initial solution.

EXPERIMENTAL

The oxidation reactions and the preparation of the distillates have been described previously[8,9]. A total volume of 15 ml are heated and 10 ml of distillate are collected.

Aeration procedure

The apparatus is similar to that described by Cox[20]. 10 ml of distillate are aerated at room temperature for 45 min into 2 ml of 1% sodium hydrogen sulphite.

The colorimetric determination of formaldehyde and acetaldehyde

The residue after the aeration procedure is diluted to 10 ml with water and the formaldehyde content determined as described below. The sulphite solution is diluted to 10 ml with water and the acetaldehyde content determined as described below.

A. Formaldehyde

Reagents: 1. Chromotropic acid reagent. This is prepared fresh before use. 0.2 g of purified chromotropic acid is dissolved in 2 ml of water and 48 ml of 13*M* sulphuric acid added; 2. 9*M* sulphuric acid.

Procedure: Into a test tube are measured 1-3 ml of solution containing up to 10 μg of formaldehyde. The volume is made up to 3 ml by the addition of water. 5 ml of chromotropic acid reagent are added and after mixing, the tube is placed in a boiling water bath for 30 min. After cooling, the mixture is diluted to 10 ml with 9*M* sulphuric acid. Readings are made against a blank at 570 mμ.

B. Acetaldehyde

Reagents: 1. concentrated sulphuric acid; 2. 20% copper sulphate solution; 3. *p*-hydroxybiphenyl reagent, 1.5 g of *p*-hydroxybiphenyl are dissolved in 10 ml of 5% sodium hydroxide and diluted to 100 ml with water.

Procedure: To 1 ml of sulphite solution, containing up to 10 μg of acetaldehyde, are added 0.1 ml of 20% copper sulphate solution followed by 6 ml of concentrated sulphuric acid. After mixing and cooling, 0.1 ml of *p*-hydroxybiphenyl reagent is added and the mixture kept at 30° for 1/2 h. The mixture is then placed in a boiling water bath for exactly 90 sec. After cooling, 7 ml of concentrated sulphuric acid are added and after mixing read against a blank at 560 mμ.

Standardisation

For standardisation purposes, the individual substances are subjected to the same procedure, except that aeration is excluded. The colorimetric reactions are therefore applied directly to the distillates.

TABLE II

THE RECOVERY OF FORMALDEHYDE AND ACETALDEHYDE AFTER AERATION

Periodate oxidation (reaction – acid)

Glucose added μg	*Rhamnose added μg*	*Glucose recovered μg*	*Rhamnose recovered μg*
100	0	92 (92%)	0
250	0	239 (96%)	0
0	100	0	94 (94%)
0	250	0	238 (95%)
100	250	91 (91%)	238 (95%)
250	100	242 (97%)	96 (96%)

Glucose added μg	*Fucose added μg*	*Glucose recovered μg*	*Fucose recovered μg*
100	250	93 (93%)	238 (95%)
250	100	241 (96%)	93 (93%)

TABLE II (continued)

Periodate oxidation (reaction – neutral)

Serine added µg	*Threonine added* µg	*Serine recovered* µg	*Threonine recovered* µg
100	0	91 (91%)	0
250	0	236 (94%)	0
0	100	0	89 (89%)
0	250	0	230 (92%)
100	250	89 (89%)	232 (93%)
250	100	238 (95%)	92 (92%)

Ninhydrin reaction

Glycine added µg	*Alanine added* µg	*Glycine recovered* µg	*Alanine recovered* µg
100	0	91 (91%)	0
250	0	232 (93%)	0
0	100	0	92 (92%)
0	250	0	234 (94%)
100	250	89 (89%)	240 (96%)
250	100	232 (93%)	91 (91%)

% Recoveries are recorded in brackets

RESULTS

The procedure involving the separation of formaldehyde and acetaldehyde from the distillates has been applied to:

1. mixtures of glucose and rhamnose or fucose allowed to react with periodic acid in an acid medium,
2. mixtures of serine and threonine allowed to react with periodate in neutral medium,
3. mixtures of glycine and alanine allowed to react with ninhydrin at pH 5.

From the results shown in the Table II it will be seen that the aeration procedure provides an efficient separation of the two aldehydes.

SUMMARY

The use of an aeration procedure for the separation and determination of formaldehyde and acetaldehyde liberated by the following reactions: (1) sugars/periodate, (2) serine and threonine/periodate, (3) glycine and alanine/ninhydrin, has been examined and shown to be satisfactory.

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Received February 7th, 1958

DETERMINATION OF URANIUM, ZIRCONIUM, MAGNESIUM AND IRON IN BISMUTH ALLOYS

by

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There has recently been considerable interest in developing chemical methods of analysis for bismuth alloys, because of the possible uses of liquid bismuth in atomic reactors.

Uranium, zirconium and magnesium are three metals which are sometimes added to liquid bismuth, and in this paper methods are described for the analysis of bismuth containing these additions. As liquid bismuth is usually contained in steel systems it is also important to know its iron content and the method described here is suitable for the amounts of iron commonly found in liquid bismuth in a steel container.

It is very important to have a sound sampling technique and there are various ways of ensuring that the sample is representative. Rapid quenching of the liquid bismuth is essential to prevent segregation of the additives and it may be necessary to filter the liquid if there has been considerable corrosion of the steel container. If there is any suspicion that segregation has occurred during the cooling of the sample it may be advisable to dissolve the whole of the sample taken and then take aliquots of this solution for the individual determinations. (In all the procedures nitric acid is used for dissolving the bismuth).

DETERMINATION OF URANIUM

Introduction

Procedures for the determination of uranium in bismuth have been described. MILNER AND EDWARDS[1] describe a method where uranium is precipitated as phosphate in presence of E.D.T.A. They claim a lower limit of 0.5% uranium, whereas we were interested primarily in the range 0.01 – 0.1% uranium. SHELTON[2] precipitates uranium with oxine in presence of E.D.T.A. but again the interest is in higher uranium contents. MILNER AND BARNETT[3] describe a method where uranium, after separation from bismuth by volatilisation of bismuth bromide and separation from iron by an ion exchange method, is determined by titration with ceric sulphate solution, after reduction in a micro lead reductor. This method is satisfactory for the range in which we are interested, but has the disadvantage of being rather tedious for routine analysis. EBERLE AND LERNER[4] describe a method where uranium is first separated from bismuth by extraction with tributyl phosphate and then determined spectrophotometrically with oxine.

We have also used an oxine spectrophotometric method, but by employing ethylenediaminetetraacetic acid (E.D.T.A.) as a complexant for bismuth (and other interfering elements), we have avoided any preliminary separation of bismuth and uranium. Briefly, the method involves solution of the bismuth alloy in nitric acid, evaporation of the bulk of the excess acid, addition of E.D.T.A. to complex the bismuth, iron, zirconium, etc., adjusting the pH to 7.0, addition of 5% oxine in alcoholic solution and extraction of the uranium oxine complex with chloroform. The uranium is then determined spectrophotometrically, measuring the absorption of the chloroform extract at 400 mμ.

Experimental

The best conditions for the extraction of uranium oxinate were studied.

Optimum pH

There is a certain amount of disagreement among previous analysts as to the best pH for carrying out this extraction, probably because different buffers were used. RULFS, LAKRITZ AND ELVING[5] use a pH of 7.0, but EBERLE AND LERNER[4] use a pH of 7.6; under the conditions of our method, maximum extraction was obtained between pH 6.5 and pH 7.5. For this reason we recommend pH 7 as a suitable pH, and obtain this with an ammonium acetate buffer.

Extraction technique

We found that under our test conditions a chloroformic solution of oxine (as recommended by previous workers[4,5]) did not extract all the uranium from the aqueous phase. Although the mechanism was not understood it appeared that the high E.D.T.A. concentration in the aqueous phase was responsible. We found, however, that if the oxine was added to the aqueous phase first, in a 5% alcoholic solution, then subsequent extraction with chloroform gave an almost quantitative recovery of uranium. By repeating the process, adding more alcoholic oxine solution and extracting again with chloroform, recovery of uranium was complete. It was found very difficult to avoid tiny droplets of the aqueous phase coming through with the chloroform extract, but if the chloroform solution was carefully decanted to a clean dry graduated flask these droplets could be removed. Addition of alcohol to attempt to clear the solution resulted only in turbidity.

Interferences

Bismuth — A calculated amount of E.D.T.A. was sufficient to complex all the bismuth and prevent the formation of bismuth oxinate.

Zirconium — When only a small excess of E.D.T.A. over and above that required to complex the bismuth was present, a gelatious precipitate was obtained on adding oxine, which was not extracted by the chloroform but interfered by partially absorbing uranium, leading to low results. When however, a considerable excess of E.D.T.A. was added this precipitate did not appear and there was no interference.

Iron, magnesium, manganese, nickel — no interference.

Procedure

0.2 g sample was dissolved in 2 ml nitric acid, and evaporated until salts crystallized out. 1 ml of hydrochloric acid was added and the solution diluted. 2.5 g of E.D.T.A. were added, followed by excess dilute ammonia. When the E.D.T.A. had completely dissolved, the pH of the solution was adjusted to 7.0 by addition of dilute acetic acid. The volume of the solution was now 50 ml (approx.), 2 ml of 5% oxine solution in alcohol were added and the uranium complex extracted with 5 ml of chloroform in a separating funnel. Another 2 ml 5% oxine was added, the extraction was repeated and then a final extraction with 5 ml of chloroform. The combined chloroform extract was transferred to a clean dry flask and made up to 20 ml with chloroform. Measurements were made on a Uvispek Spectrophotometer, wavelength 400 mμ in a 4-cm cell.

Range: 20–1000 p.p.m.

A blank on reagents was determined by using distilled water instead of sample solution.

Calibration

Uranium solution: 0.4 g Uranium dissolved in HCl and diluted to 1 litre (1 ml = 400 γ U). 50 ml of this solution diluted to a 1 litre (1 ml = 20 γ U).

Bismuth solution: 10 g of bismuth in 250 ml HCl solution (1 ml = 40 mg Bi).

Zirconium solution: 0.01 g Zr dissolved and made up to 200 ml (1 ml = 50 γ Zr).

5 ml of bismuth solution and 2 ml of zirconium solution were added to a known volume of standard uranium solution. 2.5 g of E.D.T.A. was added and the solution was adjusted to pH 7.0 with ammonia and acetic acid as described above. Extraction was then carried out as described.

A blank was carried out on the reagents and bismuth by substituting water for the standard uranium solution.

DETERMINATION OF ZIRCONIUM

Introduction

There have been no reports in the literature of any methods for determination of zirconium in bismuth. Usually a spectrographic method is employed, but it is desirable to have an alternative chemical method available. Alizarin S has been recommended by several authors, and MAYER AND BRADSHAW[6] indicate that 50 mg Bi do not interfere in their procedure for determining zirconium in magnesium alloys. We found, however, that when much larger quantities were present hydrolysis occurred with precipitation of bismuth oxychloride on diluting the colour solution. We have found that by suitable modifications of their method it can be applied to the determination of zirconium in bismuth.

Experimental

Suitable acid medium

Nitric acid is used to dissolve the bismuth, but even traces of this interfere strongly with the colour formation, and so must be removed. Sulphuric acid cannot be used, and repeated evaporation with hydrochloric acid is tedious. Fuming with perchloric acid is permissible and because the quantity of acid present in the final solution is critical the excess perchloric acid is almost completely removed by heating at 200°. (This temperature is fairly critical.) The residue is then taken up in a controlled amount of water and hydrochloric acid.

Colour development

Based on MAYER AND BRADSHAW's results and our own experiments, an acid concentration of 1.3*N* hydrochloric acid is employed (2.5 ml 11.2*N* hydrochloric acid in 21.5 ml). After formation of the colour the solution is diluted to 25 ml, so that the acidity is about 1.1*N*. At this acidity bismuth oxychloride is not precipitated. Because we do not dilute as much as MAYER AND BRADSHAW we use an 0.1% alizarin S solution instead of 0.15% to reduce the blank as much as possible. Below 0.1% the rate of colour formation drops off.

Interferences

Bismuth, under the conditions described, does not interfere. Uranium, magnesium, nickel, manganese also do not interfere. MAYER AND BRADSHAW indicate that ferric iron interfere, but no appreciable interference was given by 500 μg Fe^{+3}. This is far more than likely to be present in 0.5 g bismuth.

Procedure

The method finally adopted is as follows:

Dissolve 0.5 g bismuth alloy in 5 ml 1:1 nitric acid in a 50 ml squat beaker. Add 0.75 ml perchloric acid and evaporate the solution to fuming. Fume until salts separate, and remove the excess perchloric acid by fuming at 200° on a thermostatically controlled hot plate for 15 min. Cool, add 5 ml of water from a burette to dissolve the salts, and transfer the solution to a 25-ml flask. Add 9 ml of water (from a burette) to rinse out the beaker, adding the washings to the 25-ml flask. Add 2.5 ml concentrated hydrochloric acid and 5 ml of reagent to the flask. Immerse the flask in a boiling water bath for 3 min, cool, and make up to 25 ml. Measure the colour on a Uvispek spectrophotometer at 560 mμ wavelength, 4-cm cells, after standing 15–30 min.

Calibration

Pure bismuth and standard zirconium solution are treated by the above method and a calibration curve constructed.

Reagents

1. Alizarin S reagent, dissolve 0.5 g reagent in hot water, filter on a pulp pad, cool, and make up to 500 ml.

2. Standard zirconium solution, dissolve 0.5 g zirconium in a mixture of nitric acid and hydrofluoric acid. Add 10 ml of perchloric acid and take to fuming. Dilute the perchloric acid solution of zirconium with water, add 70 ml of perchloric acid and then dilute to 500 ml. This gives a solution approximately 1.5*N* perchloric acid. (1 ml zirconium solution = 1000 γ Zr.)

3. Dilute standard zirconium solution, 10 ml above solution diluted to 200 ml (1 ml = 50 γ Zr).

DETERMINATION OF MAGNESIUM

Introduction

No method has been described for the determination of magnesium in bismuth alloys in the literature. It appeared to be impossible to determine magnesium without preliminary separation of bismuth and other metals, and some thought was given to this problem. A number of methods appeared possible. Chromatographic and ion exchange methods, volatilisation of bismuth bromide, precipitation of bismuth as sulphide, oxychloride or oxycarbonate have all been described and have their various advantages and disadvantages. None of them, however, are rapid methods and we have investigated a double solvent extraction method which has the advantage of rapidity of manipulation and clean separation. Briefly bismuth is first extracted as iodide with methyl isobutyl ketone in acid solution and then other metals (uranium, zirconium, iron, nickel, manganese, residual bismuth, etc.) with oxine at pH 6.5.

Experimental

Separation of bismuth

The extraction of bismuth as bismuth iodide from acid solution by methyl isobutyl ketone has been proposed as a spot test for small amounts of bismuth[7]. Investigation showed that this extraction could be employed on a macroscale and that over a considerable range of acidity (0.8*N* to 3.0*N*) more than 99% of the bismuth can be removed from the aqueous phase in one extraction. Thus, two extractions of 0.4 g bismuth only leave μg amounts in the aqueous phase.

Separation of other impurities

Here again a solvent extraction procedure was chosen for rapidity. Oxine (8-hydroxyquinoline) forms complexes in neutral solution with all the anticipated interfering metals and it was found that the complexes could all be extracted with chloroform. Uranium, zirconium, iron, last traces of bismuth, manganese and nickel were all quantitatively removed under the conditions chosen'

Determination of magnesium

A number of methods have been suggested for magnesium, mostly spectrophotometric procedures employing titan yellow, magneson, etc. In view of the presence of excess oxine in the solution, a method described by DAVIDSON[8] was preferred, where oxine is used to precipitate magnesium as oxinate, and the oxine in the precipitate determined spectrophotometrically after solution in acid. To precipitate magnesium oxinate in the solution after extraction of the other metals it is only necessary to raise the pH by addition of ammonia and to add more oxine.

Procedure

Dissolve 0.400 g bismuth in 5 ml nitric acid. Add 2 ml perchloric acid and fume vigorously. Take up the residue in 10 ml 20% hydrochloric acid, add 10 ml 20% ammonium iodide and transfer to a separating funnel with 2 × 5 ml water washings. Add 40 ml methyl isobutyl ketone and extract the bismuth iodide. Run off the aqueous layer carefully into another separating funnel and extract with a further 40 ml methyl isobutyl ketone. Transfer the aqueous layer to another separating funnel, add 2 ml 2% oxine solution in $2N$ acetic acid and add ammonia dropwise to pH 6–7. Add 20 ml chloroform and extract the precipitated oxines (U, Zr, Fe, Ni, Mn and residual Bi). Run off and reject the chloroform layer, extract with another 20 ml chloroform and again run off and reject. Transfer the aqueous solution (containing the Mg) back to a beaker and evaporate to about 20 ml. Cool, add 1 ml 2% oxine in $2N$ acetic acid and add 30 drops (*ca.* 1 ml) ammonia. (Check pH > 10). Transfer to a centrifuge tube and digest for ½ h on water bath. Allow to cool for ½ h and centrifuge. Reject the supernatant liquid, wash the precipitate 3 times with 3 ml 4% ammonia. Dissolve the precipitate in 6 drops hydrochloric acid, add water, transfer to a 20-ml graduated flask and dilute to 20 ml with water. Measure the absorption on a Hilger Uvispek Spectrophotometer (or similar instrument) at 365 mμ, 1-cm cells.

Calibration

Prepare a solution containing 50 μg Mg/ml. Take 0, 1, 2, 3, 4, 5 ml of this solution. Add 10 ml 20% hydrochloric acid and 10 ml 20% ammonium iodide and treat as in the preceeding method.

DETERMINATION OF IRON

Introduction

HOLMES[9] describes a method for the determination of iron in bismuth where *o*-phenanthroline is used as the reagent and E.D.T.A. is used to complex bismuth. We have experimented with 4,7-diphenyl phenanthroline as a reagent and found that in presence of E.D.T.A. iron is not completely reduced by hydroxylamine hydrochloride. It is probable that the procedure as described by HOLMES allows for this by preparing the calibration graph is an identical manner to that employed for unknown alloys. However, we preferred to examine an alternative procedure. In some unpublished work on the determination of very small amounts of cobalt in steel and nickel, where the cobalt is finally determined as cobalt thiocyanate after extraction by methyl isobutyl ketone, we discovered that iron thiocyanate is also very readily extracted by this solvent, and that moreover, the intensity of the colored iron complex is very much higher in ketonic solution that in aqueous solution. Since iron thiocyanate is formed in acid solution there is no danger of bismuth hydrolysing, or any need to complex it. HOLMES states that bismuth interferes in the thiocyanate method, but we have found that although bismuth gives a yellow colour in aqueous solution, this bismuth complex is not extracted by methyl isobutyl ketone and therefore does not cause any interference if there is excess thiocyanate present.

Experimental

Conditions for the extraction

Acidity. The optimum acidity for development of the iron thiocyanate complex was studied in sulphuric, perchloric and hydrochloric acid solutions. Perchloric acid was found to be the most promising, but it was found that bismuth thiocyanate was precipitated in presence of much perchloric acid. However, a small amount of perchloric acid was not harmful, and it was found that if the bismuth was dissolved in nitric acid, fumed with perchloric acid and finally hydrochloric acid added to give an acidity of *ca.* 1.2N the extraction was very satisfactory.

Thiocyanate concentration. The concentration of thiocyanate is important and there must be sufficient to completely complex the bismuth (the bismuth complex is probably $(NH_4)_3[Bi(CNS)_6]$). It is advisable to maintain a fairly accurately measured thiocyanate concentration but it is not as critical as when carrying out iron thiocyanate determination in the aqueous phase[10]. 2.5 g ammonium thiocyanate is added for 0.5 g bismuth. It was interesting to note that the slope of the calibration graph was steeper when bismuth was present; this suggests that the compound extracted may contain bismuth as well as iron, with a more intense colour than the normal iron thiocyanate complex.

Interferences

As previously mentioned, bismuth does not interfere. Uranium thiocyanate is not entirely stable at the acidity chosen and in any case does not give any absorption at the wavelength used for measurement. None of the other metals likely to be present interfere. Cobalt thiocyanate would be extracted under the conditions chosen but would have its peak absorption at a different wavelength and only very large amounts would interfere.

Purification of reagents

It was found necessary to purify some of the reagents. The reagents were purified as follows:

Nitric acid — redistilled.
Perchloric acid — grade chosen low in iron.
Methyl isobutyl ketone — redistilled.
Ammonium thiocyanate reagent — 20 g ammonium thiocyanate dissolved in water and made up to 80 ml. Add 2.5 ml N hydrochloric acid. Extract with 2 × 10 ml portions of redistilled methyl isobutyl ketone.

Using these purified reagents a blank equivalent to 1–2 μg iron was obtained, which for many analyses could be neglected.

Procedure

0.5 g bismuth is dissolved in 1 ml nitric acid and 2 ml of water. After solution is completed, 1.5 ml perchloric acid is added, and the solution evaporated to vigorous fuming to remove the nitric acid. The sample is cooled, dissolved in 12 ml water, and transferred to a 150-ml capacity separating funnel, the beaker being washed out with a further 4 ml water and the washings added to the funnel. 3 ml concentrated hydrochloric acid is added followed by 10 ml of ammonium thiocyanate reagent. The iron thiocyanate complex is extracted with 2 × 5 ml portions of methyl isobutyl ketone. The extracts are transferred to a 20 ml flask and made up to 20 ml with methyl isobutyl ketone. The absorbance is measured in 2-cm cells, Ilford spectrum filters No. 603, water setting 1.0-(Spekker absorptiometer).

Range: 0—80 p.p.m. Fe.

Calibration

Iron solution: 1 g Fe was dissolved in hydrochloric acid and diluted to 1 litre (1 ml = 1000 γ Fe). 10 ml of this solution was diluted to 1 litre (1 ml = 10 γ Fe).

Bismuth solution: 8.33 g (spec. pure) bismuth was dissolved in nitric acid and diluted to 50 ml. 3-ml aliquots of this bismuth solution, together with different amounts of added iron solution, were treated as in the above method and a calibration curve constructed.

A blank was carried out using bismuth solution without added iron.

ACKNOWLEDGEMENT

The authors acknowledge their indebtedness to their colleagues in the Research Laboratory for encouragement and assistance in this work.

SUMMARY

Uranium in bismuth alloys is determined by a procedure where E.D.T.A. is added to complex bismuth and other metals and uranium oxinate is extracted by chloroform and determined spectrophotometrically. Zirconium is determined spectrophotometrically using alizarin S as reagent under carefully controlled conditions of acidity and time of colour formation. Magnesium is determined indirectly by measuring the absorption of oxine spectrophotometrically after precipitating the magnesium oxinate complex and redissolving. Bismuth is first separated by extraction of its iodide complex with methyl isobutyl ketone, and other interfering metals by extraction of their oxinate complexes at pH 6.5. Iron is determined as its thiocyanate complex after extraction with methyl isobutyl ketone, bismuth thiocyanate remaining in the aqueous phase.

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Received February 13th, 1958

THE SPECTROPHOTOMETRIC DETERMINATION OF COMPLEXING AGENT IN A POLYNITROAROMATIC MOLECULAR COMPOUND

by

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Conversion of a polynuclear aromatic hydrocarbon (or its simple derivative) to a crystalline molecular compound with a polynitroaromatic complexing agent, such as 1,3,5-trinitrobenzene (TNB), picric acid (2,4,6-trinitrophenol, TNP), or 2,4,7-trinitrofluorenone (TNF), is commonly used for isolation, purification, and identification of the hydrocarbon. A favorite procedure for quantitative determination of TNP in such picrates is titration with standard base[1], but this method is not applicable to samples containing TNB, TNF, or other neutral complexing agents. Titration of nitro groups on the complexing agent[2] by means of $TiCl_3$, moreover, is complicated by the necessity of operating in an oxygen-free atmosphere. A spectrophotometric method for determination of the molecular weight of an amine picrate or a hydrocarbon picrate by single measurement of absorbance at 380 mμ has been described[3]. FRIEDEL AND ORCHIN[4] imply that the molar composition of TNB, TNP, and TNF molecular compounds can be ascertained by a similar method. The present report concerns the use of a modified spectral procedure to determine the percentage of complexing agent present in such molecular compounds of naphthalene and its derivatives.

EXPERIMENTAL

Naphthalene, crystalline substituted naphthalenes, TNB, TNP, and TNF were recrystallized to constant m.p. Liquid substituted naphthalenes were freshly distilled. Molecular compounds were prepared from these reagents and recrystallized to constant m.p. by previously described methods[5–7]. Standard solutions ($3 \cdot 10^{-3}$ to $7 \cdot 10^{-5} M$), prepared by dissolving weighed amounts of either the complexing agent alone or the molecular compound alone in glacial acetic acid and diluting to volume with the same solvent, were measured for absorbance at intervals of 5 mμ over a suitable range of wavelengths by means of a Beckman DU spectrophotometer using a tungsten filament as source and Corex cuvettes. The ratio, r, of the absorbance of the solution of the molecular compound to that of its complexing agent was calculated for each wavelength λ. In each case a range of λ (usually 330–370 mμ for TNB, TNP, and their molecular compounds or 360–400 mμ for TNF and its molecular compounds) was selected such that it provided reasonably constant values for r. At shorter λ, where it is presumed that absorption by the complexed moiety occurs, r was found to vary with λ. Correspondingly, in the selected region (where absorption is considered to arise only from the presence of the complexing agent) one has the relationship $x = 100\, r_{\text{ave}} \left(\frac{C_c}{C_m}\right)$, where $x = \%$ of complexing agent present in the sample of molecular compound, r_{ave} is the average value of r, C_c is the concentration (in wt. per unit volume of solution) of the complexing agent present in solution by itself, and C_m is the corresponding concentration for the molecular compound in its solution. Typical data are recorded in Table I and results are given in Table II.

TABLE I

TYPICAL DATA FOR ABSORBANCES OF SAMPLES OF SOLUTIONS OF COMPLEXING AGENTS AND CORRESPONDING MOLECULAR COMPOUNDS

λ *mμ*	*Absorbance* *TNB*	*Absorbance* *1-Bromonaphthalene-TNB*	*r*	λ *mμ*	*Absorbance* *TNF*	*Absorbance* *Naphthalene-TNF*	*r*
330	0.850	0.900	1.06	360	0.905	0.975	1.08
335	0.805	0.835	1.04	365	0.835	0.895	1.07
340	0.748	0.778	1.04	370	0.677	0.728	1.08
345	0.690	0.718	1.04	375	0.597	0.640	1.07
350	0.612	0.636	1.04	380	0.494	0.538	1.09
355	0.532	0.555	1.04	385	0.398	0.432	1.08
360	0.453	0.472	1.04	390	0.318	0.344	1.08
365	0.378	0.395	1.04	395	0.228	0.249	1.09
370	0.309	0.324	1.05	400	0.153	0.167	1.09
		r_{ave}	1.04			r_{ave}	1.08

C_c = 0.625 g/l
C_m = 1.271 g/l

C_c = 49.2 mg/l
C_m = 75.7 mg/l

TABLE II

DETERMINATION OF % OF COMPLEXING AGENT PRESENT IN MOLECULAR COMPOUNDS

Complexing agent	*Moiety complexed*	*M.p. of complex °C*	*% of complexing agent* *calcd.*	*% of complexing agent* *found*	*Absolute error (%)*
TNB	naphthalene	152–153	62.5	64.1	+1.6
TNB	1-bromonaphthalene	137–138	50.7	51.2	+0.5
TNB	1-methylnaphthalene	145–146	60.0	61.0	+1.0
TNB	2-methylnaphthalene	122.5–123.5	60.0	61.4	+1.4
TNB	3-methyl-2-(1-naphthyl)-1-cyclohexene[6]	89–110	49.0	51.2	+1.2
TNB	3-methyl-2-(1-naphthyl)-1-cyclopentene[6]	95–96	50.7	52.8	+2.1
TNB	3-methyl-2-(2-naphthyl)-1-cyclohexene[6]	83–84	49.0	50.7	+1.7
TNF	naphthalene	150–151	71.2	70.2	—1.0
TNF	1-methylnaphthalene	161–162	69.0	69.5	+0.5
TNF	2-methylnaphthalene	124–125	69.0	68.7	—0.3
TNF	3-methyl-2-(2-naphthyl)-1-cyclopentene[6]	123–124	60.2	60.4	+0.2
TNF	1-(5-methyl-1-naphthyl)-cyclopentene[7]	103–119	60.2	59.5	—0.7
TNP	naphthalene	149–150.5	64.2	63.9	—0.3
TNP	1-methylnaphthalene	139–140	61.8	61.7	—0.1
TNP	1-(5-methyl-1-naphthyl)-cyclohexene[7]	96–111	50.8	51.2	+0.4

DISCUSSION

In our studies it was always assumed that the molar ratio of complexing agent to complexed moiety in the molecular compound was 1:1 and an effort was made to prepare corresponding solutions in such manner as to contain nearly equal concentrations of the pertinent absorbing species, *i.e.* the complexing agent. This assumption is not necessary for successful use of the method. However, that all of our compounds were indeed of the 1:1-type is apparent from Table II where the percentages of complexing agent found are compared with those calculated for such a ratio. It is interesting that this molar ratio exists even in three compounds having wide (but constant) melting ranges. In fact, our method was first devised to check the composition of such widely melting molecular compounds which occur rather frequently in organic chemistry. The result would seem to indicate that regular packing of the complexing agent and the complexed moiety into a crystal lattice is not a requirement for the separation of a stoichiometric solid molecular compound of the polynitroaromatic type.

The concentration range of *ca.* 10^{-3} to $10^{-4}M$ for these studies is significant for two reasons. First, the solutions are sufficiently dilute to ensure effectively complete dissociation of the molecular compound[5,8] and, second, they are readily measurable on the spectrophotometer.

When compared to microanalysis for nitrogen, our spectrophotometric method appears to offer advantages of greater simplicity, lessened cost, and at least equal accuracy for TNB, TNF, and TNP molecular compounds. Excluding 1-bromonaphthalene·TNB the molecular formulas of the compounds in Table II range from $C_{29}H_{21}N_3O_7$ (8.03% N) to $C_{16}H_{11}N_3O_6$ (12.31% N). The usually acceptable absolute error of ± 0.40% in N then corresponds to *ca.* 3-5% relative error in the analysis. The relative error in values in Table II is no greater than 4.1% and averages 1.5%. On the other hand, we believe that titration offers a more facile and, perhaps, more accurate method (as compared to spectrophotometry) for quantitative analysis of TNP in picrates.

ACKNOWLEDGEMENT

We gratefully acknowledge financial support of this work by the Office of Ordnance Research, U. S. Army, under contract number DA-04-200-ORD-176.

SUMMARY

A spectrophotometric method for quantitative determination of complexing agent in polynitroaromatic molecular compounds of naphthalene and its derivatives is described. The procedure involves comparison of the absorbances of solutions of the molecular compounds and its complexing agent over a range of wavelengths where absorption by the complexed moiety is negligible. An absolute accuracy of 2% or less is indicated.

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Received February 1st, 1958

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

I. BISMUTHIOL I AS AN ANALYTICAL REAGENT

by

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Bismuthiol I (2,5-dimercapto-1,3,4-thiodiazole) was introduced by DUBSKY[1] as a spot-test reagent, which was later utilized by MAJUMDAR[2] for the colorimetric determination of bismuth. RAY AND GUPTA[3] employed it for the separation of copper and lead from other elements.

The reagent Bismuthiol I shows a high absorption below 400 mμ without having any sharp absorption peak for the colour system with palladium. Measurements are found to be suitable at 400 mμ to 410 mμ, since in that region difference in absorption measured against the reagent blank is maximum. The colour develops instantaneously and is independent of pH, though it is not very stable below pH 6 where the optical density increases with time owing to aerial oxidation. The palladium-bismuthiol I complex is fairly soluble in water and the sensitivity of the colour reaction at 400 mμ or 410 mμ is 0.015 μg palladium per cm² (SANDELL[7]). The composition and the dissociation constant of the complex have been elucidated by JOB's method of continuous variation[4] and found to be $Pd(C_2N_2S_3)$ with an average instability constant of $3.2 \cdot 10^{-5}$ at 25°.

EXPERIMENTAL

Apparatus and solution

A spectrophotometer, Unicam SP 600, with 1.00-cm cell was used for all absorbance measurements and the pH of the solutions prepared was measured with a Cambridge pH indicator.

A standard solution of palladium chloride was prepared from 'Specpure' palladium chloride of Johnson and Matthey and its palladium content per ml was determined with dimethylglyoxime and confirmed with Bismuthiol II[5]. Weaker solutions were obtained by dilution.

Solutions of cations and anions were prepared from their reagent-grade salts and a 1% (w/v) solution of complexone III was used as a complexing agent.

The organic solvents used were all of *pro analysi* variety except ethyl alcohol and pyridine which were distilled twice before use.

Bismuthiol I of m.p. 168° was prepared according to the method of BUSCH[6] and a 0.25 % solution of the reagent was obtained by dissolving 0.25 g in a minimum quantity of 0.1N caustic soda solution and diluting with water to 100 ml.

For the study of the composition and the dissociation constant of the complex, equimolecular and non-equimolecular solutions of palladium and the reagent were prepared.

Colour reaction

Bismuthiol I reacts rapidly with palladium in both acid and alkaline media, to give a red colour or a red precipitate, dependent on the palladium concentration. The palladium complex is somewhat soluble in water and in solvents like acetone, methyl alcohol, ethyl alcohol, dioxane and methyl cellosolve. A sample containing only 4 μg of palladium per ml showed a deviation of 1-2 % within half an hour due to instability of the coloured product in aqueous phase. This is easily avoided by the addition of ethyl alcohol, acetone or methyl cellosolve to the extent of only 10% (v/v) of the total volume. Complexone III, used to mask the effect of interfering ions, is tolerated up to a maximum of 100 mg in a volume of 25 ml.

In Fig. 1 the absorbance curves are recorded of (1) the palladium complex against the reagent solution, (2) the palladium complex against water and (3) the reagent solution against water. The curves indicate that the optical density of the reagent is negligible at and above 400 mμ. The palladium complex shows no sharp peak of maximum absorption but maintains the same absorption at 400–410 mμ. Consequently all measurements were made at 400 mμ.

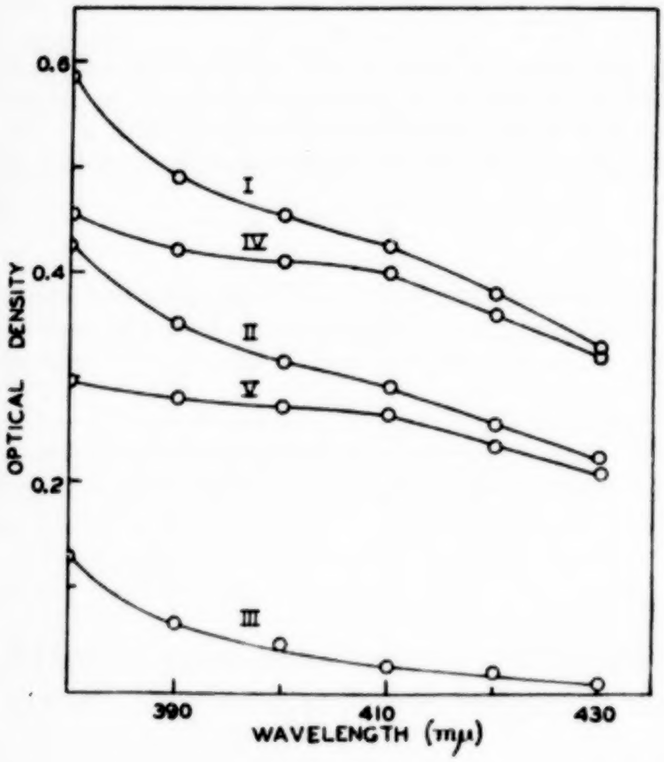

Fig. 1. Absorption regions of the colour system at pH 7.0. The system contained, besides palladium, 4 ml of reagent and 2.5 ml ethyl alcohol in a total volume of 25 ml. I: 6 μg Pd/ml; II: 4 μg Pd/ml; III: without Pd; IV: corrected value (I—III); V: corrected value (II—III).

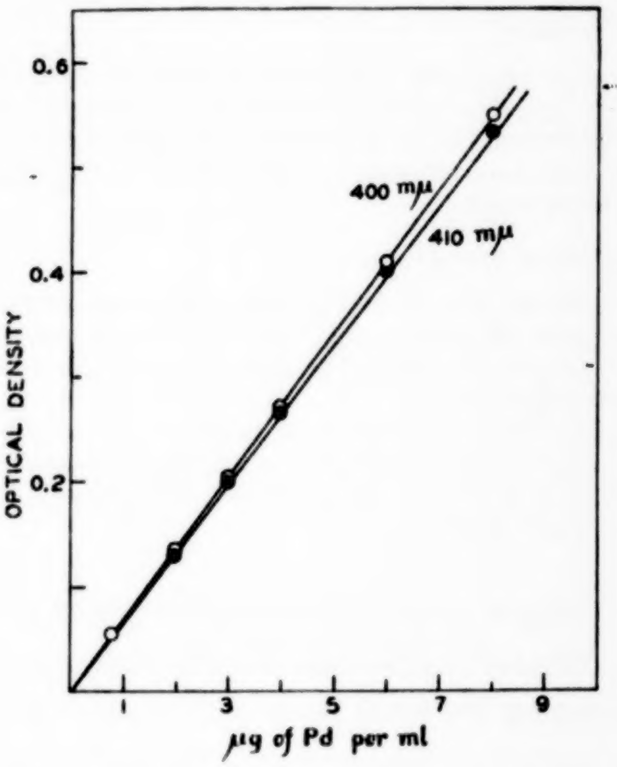

Fig. 2. Study of Beer's law. 4 ml reagent, 2.5 ml ethyl alcohol in a total volume of 25 ml, pH 6.0.

Effect of solvent

A study of the effect of organic solvents, such as ethyl alcohol, acetone, dioxane, pyridine and methyl cellosolve, revealed that except for ethyl alcohol, all the other solvents reduce the colour intensity. Since pure ethyl alcohol has a considerable absorption at 400–410 mμ and also a salting effect, a dilute solution (total vol. 25 ml) with only 10% (v/v) of the alcohol was tested and found to be suitable for all subsequent measurements.

Effect of reagent

Absorption measurements at 400 mμ or 410 mμ of a number of solutions containing different amounts of reagent (1–10 ml), each with 4 μg of palladium per ml and maintained at a pH of about 8.0, showed that the colour system is independent of the quantity of the reagent and hence for subsequent measurements, 4.0 ml of the reagent solution was added to the palladium solution, the volume then being made up to 25 ml as stated above.

Effect of pH, time and temperature

The pH of the palladium solution was adjusted to various values between 2 and 10 by dilute hydrochloric acid or ammonia after the addition of the reagent solution. After dilution to 25 ml, the optical density of every solution was measured against a reagent blank. It was observed that at a pH between 6 and 10, the deviation is less than 1% in 24 h; after more than 48 h the change was 5–6%.

The colour system was found to be stable at a temperature between 20 and 30°, but at 35° it showed a deviation to the extent of about 1%.

Beer's law and sensitivity

That the colour system when measured against a reagent blank, follows Beer's law for the concentration range from 0.8 μg to 8.0 μg of palladium per ml is evident from the fact that when the optical densities at 400 mμ or 410 mμ, are plotted against the respective concentrations, a straight line is obtained which passes through the origin; the optical density for 4 μg of palladium per ml is 0.270 and 0.265 at 400 mμ and 410 mμ respectively (*cf.* Fig. 2).

The sensitivity of the colour system is 0.08 μg palladium per cm^2 (practical); 0.015 μg palladium per cm^2 at 400 mμ or 410 mμ (SANDELL[7]).

Procedure

The pH of the palladium solution is adjusted to any value between 6 and 10 after the addition of 4 ml of the reagent solution. 2.5 ml ethyl alcohol and a few ml of water are added to make up the volume to 25 ml. After thorough mixing, a portion of the solution is transferred into a 1-cm absorption cell and its optical density measured at 400 mμ against a reagent solution prepared in the same way.

Effect of diverse ions

An ion, the effect of which is to be studied, is added to the palladium solution present in a 25-ml volumetric flask. 5 ml of the solution of complexone III and 4 ml of the reagent solution are added in succession before the adjustment of pH and then the procedure followed is exactly the same as described above.

An ion is considered to interfere if the absorbance differs by more than 0.005 from the value obtained with palladium alone. The tolerance limits of the diverse ions are summarized in Table I. Ions of platinum, gold, copper, chromium, iron, mercury, silver, thallium, uranium, vanadate and cyanide interfere.

Composition of the palladium complex in solution

Mixtures of equimolecular solutions of palladium and the reagent were prepared, keeping the total volume constant, and their absorbances were measured at 400 mμ,

TABLE I

Pd taken, 100 μg

Ions	*Maximum amount of ion tolerated, μg*	*Ion/Pd ratio at maximum tolerance limit*	*Ions*	*Maximum amount of ion tolerated, μg*	*Ion/Pd ratio at maximum tolerance limit*
Co^{+2}	50.0	12.5	Cl^-	250.0	62.5
Mn^{+2}	100.0	25.0	F^-	200.0	50.0
Ni^{+2}	50.0	12.5	Br^-	200.0	50.0
Zn^{+2}	100.0	25.0	I^-	200.0	50.0
Ca^{+2}	200.0	50.0	NO_3^-	250.0	62.5
Ba^{+2}	200.0	50.0	NO_2^-	250.0	62.5
Sr^{+2}	200.0	50.0	SO_4^{-2}	250.0	62.5
Mg^{+2}	200.0	50.0	$S_2O_3^{-2}$	200.0	50.0
Al^{+3}	100.0	25.0	PO_4^{-3}	200.0	50.0
Be^{+2}	50.0	12.5	AsO_4^{-3}	200.0	50.0
Zr^{+4}	100.0	25.0	AsO_3^{-3}	200.0	50.0
TiO^{+2}	50.0	12.5	BO_3^{-3}	200.0	50.0
Th^{+4}	160.0	40.0	MoO_4^{-2}	200.0	50.0
Cd^{+2}	100.0	25.0	WO_4^{-2}	200.0	50.0
Pb^{+2}	160.0	40.0	Acetate	250.0	62.5
Bi^{+3}	100.0	25.0	Formate	250.0	62.5
Sn^{+4}	50.0	12.5	Oxalate	200.0	50.0
Ru^{+3}	8.0	2.0	Benzoate	200.0	50.0
Os^{+4}	10.0	2.5	Salicylate	200.0	50.0
Ir^{+4}	10.0	2.5	Citrate	250.0	62.5
Rh^{+3}	4.0	1.0	Tartrate	250.0	62.5

at which wavelength the reagent if present in small amounts has negligible absorption. The data are represented graphically in Fig. 3, where the corrected and the uncorrected optical densities are plotted against the composition of the mixtures; corrected values are obtained by measuring the colour system against a solution containing palladium only, which shows some absorption. The optical densities of these mixtures of equimolecular solutions lead one to the conclusion that the complex between palladium and the reagent is formed when the reactants are in the ratio of 1:1 as the maximum is obtained at that ratio.

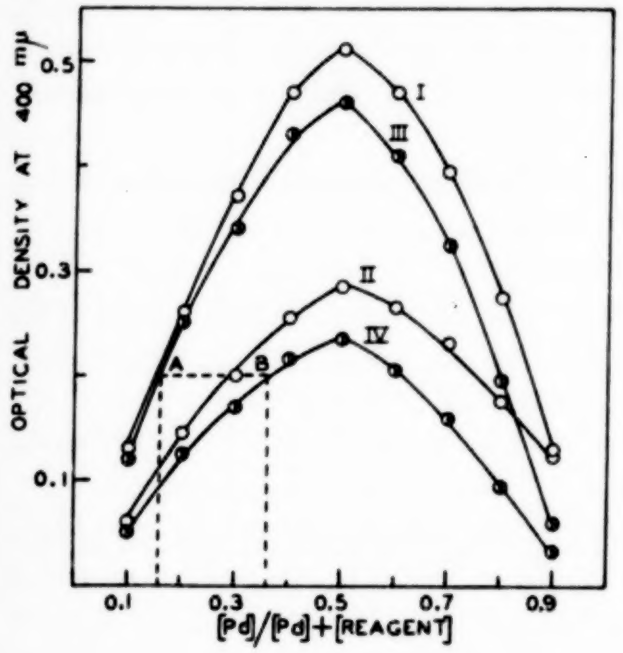

Fig. 3. Mixtures of equimolecular solutions. I: $1.88 \cdot 10^{-4} M$; II: $0.94 \cdot 10^{-4} M$; III and IV: corrected values.

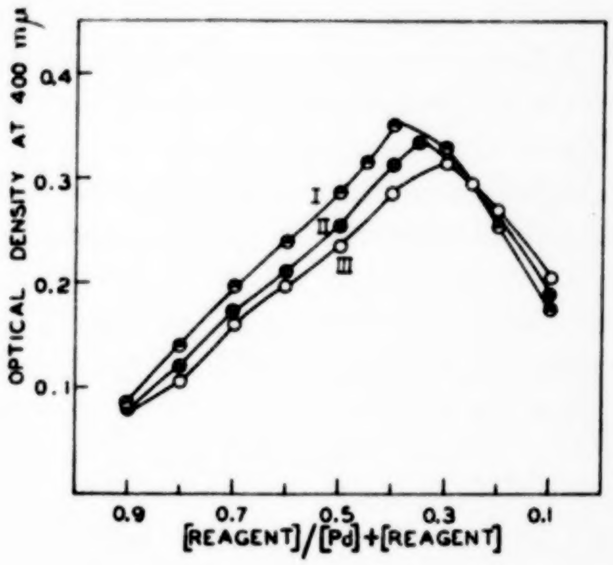

Fig. 4. Mixtures of non-equimolecular solutions. I: $0.94 \cdot 10^{-4} M$ Pd and $1.88 \cdot 10^{-4} M$ reagent; II: $0.94 \cdot 10^{-4} M$ Pd and $2.82 \cdot 10^{-4} M$ reagent; III: $0.94 \cdot 10^{-4} M$ Pd and $3.76 \cdot 10^{-4} M$ reagent.

Dissociation and formation constants of the complex in solution

The formation and dissociation constants have been calculated from Fig. 3. It may be assumed that at the points A and B of the ascending portion of the curves III and IV, the observed optical density (0.20) is mainly due to the colour of the complex; there the amount sof the complexes are identical. For the system $m\text{A} + n\text{B} = \text{A}_m \text{B}_n$, where $m = n = 1$, the formation constant is

$$K_f = \frac{x}{(a - x)(b - x)} \quad \dots\dots\dots\dots\dots\dots \quad (1)$$

in which x is the concentration of the complex, a and b are the initial concentrations of palladium and bismuthiol I respectively. With the two concentrations a_1, a_2 and b_1, b_2 of the reactants, for which the optical density is the same, the values due to x_1 and x_2 are the same, therefore,

$$K_f = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)} \quad \dots\dots\dots \quad (2)$$

$$\text{or } x = \frac{a_1 b_1 - a_2 b_2}{(a_1 + b_1) - (a_2 + b_2)} \quad \dots\dots\dots\dots\dots \quad (3)$$

References p. 376

The value of K_f is found from equation (1) by substituting the value of x as obtained from equation (3); thus the formation and dissociation constants can be calculated, they were found to be $2.33 \cdot 10^5$ and $4.29 \cdot 10^{-5}$ respectively.

From the absorption data (Fig. 4) of the mixtures of non-equimolecular solutions the dissociation constant (K_d) has also been calculated from the equation:

$$K_d = \frac{C^{(m+n-1)} \times p^{(n-1)} \times [(pm+n)x-n]^{(m+n)}}{m^{(n-1)} \times n^{(m-1)} \times (p-1)^{(m+n-1)} \times [n-(m+n)x]} \quad \ldots\ldots \quad (4)$$

in which m and n are molecular ratios of palladium and bismuthiol I in the complex, C is the molar concentration of palladium, p is the ratio of the molar concentration of the reagent to palladium and x is the ratio of the reagent to reagent plus palladium to give the maximum colour.

The values of m and n being 1, the dissociation constant is calculated by substituting in equation (4) the values of x, p and C as given below:

Curve	*Conc. of Pd* $\times 10^4 M$	*Conc. of bismuthiol I* $\times 10^4 M$	x	p	$K_d \times 10^5$
I	0.94	1.88	0.40	2	1.88
II	0.94	2.82	0.35	3	2.50
III	0.94	3.76	0.30	4	1.96

K_d (mean) $= 2.11 \cdot 10^{-5}$

SUMMARY

The reagent, bismuthiol I, has been successfully utilized for the spectrophotometric determination of palladium. The colour reaction is instantaneous and the system is stable for at least 24 hours in the pH range 6 to 10 but shows no sharp peak of maximum absorption. The system obeys Beer's law at a palladium concentration of 0.8 μg to 8.0 μg per ml at any wavelength between 400 mμ and and 410 mμ, giving a sensitivity of 0.08 μg of palladium per cm² (practical); 0.015 μg of palladium per cm² (SANDELL). Ethyl alcohol stabilizes the system against any deviation due to appearance of turbidity. A large excess of the reagent and almost all the cations and anions, except platinum, gold, copper, chromium, iron, mercury, silver, thallium, uranium, vanadate and cyanide, do not interfere. By applying JOB's method of continuous variation it was found that the complex contains the reactants in 1:1 ratio and that the average value of the dissociation constant of the complex is $3.2 \cdot 10^{-5}$ at 25°.

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Received January 27th, 1958

EMPLOI DU „CADION" EN CHIMIE ANALYTIQUE

I. UN MICRODOSAGE SPECTROPHOTOMÉTRIQUE DU CADMIUM

par

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INTRODUCTION

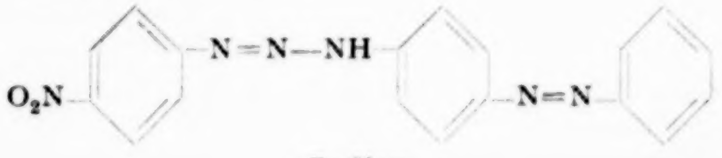
L'intérêt du microdosage de l'ion cadmium est évident dans des domaines très divers. Une revue a été faite en 1951 des diverses microméthodes par FABRE, TRUHAUT ET BOUDENE[1], qui ont eux-mêmes exposé un microdosage néphèlométrique par précipitation à l'état d'iodocadmiate de brucine. Des améliorations de la méthode à la dithizone ont été apportées par SHIRLEY, BENNE ET MILLER[2] puis par SALTZMAN[3]. Ce dernier auteur prétend doser 0.05 μg de cadmium dans 15 ml. Il n'en reste pas moins que cette méthode présente l'inconvénient d'un manque de spécificité.

WADELIN ET MELLON[4] ont proposé un microdosage spectrophotométrique du cadmium par *l'ortho*-phénanthroline dans l'ultra-violet à 241 mμ, mais la méthode n'a aucun caractère général car de nombreux ions minéraux sont absorbants à cette longueur d'onde, et par ailleurs des ions courants (Fe^{+2}, Zn^{+2}) interfèrent au point de rendre tout dosage impossible.

Les techniques proposées par SWEETSER ET BRICKER[5] (spectrophotométrie ultraviolette du versénate), RULFS *et al.*[6] (gravimétrie du thiourée-reineckate de cadmium) et par EVCIM ET REBER[7] [fluorométrie du complexe Cd-2-(*o*-hydroxyphényl)-benzoxazole] sont plus des semi-microméthodes que des microméthodes puisqu'elles indiquent des dosages de cadmium sur des prises d'essai de l'ordre du milligramme.

Étudiant spécialement le dosage du cadmium dans les zincs et les alliages antifrictions à base de zinc, JEAN[8] a présenté la revue de la question et procédé à une étude expérimentale critique des diverses méthodes, à la suite de laquelle il retient particulièrement le dosage néphèlométrique à la β-naphtoquinoléine.

Le *p*-nitrobenzènediazoaminobenzène-*p*-azobenzène proposé en 1937 sous le nom de „Cadion" par DWYER[9] pour la détection de Cd^{+2} par stilliréaction sur papier filtre n'a, semble t'il, pas été appliqué au dosage du cadmium; l'auteur pensait d'ailleurs que la réaction du cadmium sur les composés triazènes était d'ordre catalytique et ne se prêtait pas au dosage[10].



Cadion

La préparation du cadion et sa purification sont indiquées par DWYER[9], puis sont envisagées de nouveau dans un travail de FISCHER, ESTES ET ROSE[11].

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Le réactif se présente sous forme d'une poudre brune, fondant à +197° avec décomposition. Le cadion est rapidement altéré par les acides, il se dissout aisément dans les solutions alcalines alcooliques en produisant une couleur violet-pourpre. Lorsqu'on ajoute une trace de sel de cadmium à une telle solution, le colorant est adsorbé sur l'hydroxyde $Cd(OH)_2$, conférant à ce dernier une coloration rose-saumon. Lorsqu'il s'agit de faibles quantités de Cd^{+2} il ne se produit aucun précipité et on observe seulement le changement de coloration de la solution.

Dans les mêmes conditions Mg^{+2} donne une laque bleue, Ag^+ et Hg^{+2} donnent des réactions semblables au Cd^{+2}; enfin CN^- inhibe la réaction Cd–Cadion.

Pour la détection du Cd^{+2} par stilliréaction sur papier filtre, DWYER ajoutait du sel de Seignette afin d'empêcher la précipitation d'hydroxydes gênants (Cu, Ni, Cr, Fe, Co et Mg). Aucun autre ion étudié n'était gênant, la limite a été trouvée pour une goutte de solution à 0.5 μg Cd/ml.

Après étude de la réaction Mg–Cadion (inhibée par l'ion tartrique, mais pas par CN^-), DWYER a proposé[12] deux autres triazènes: le *p*-nitronaphtalène-diazoaminobenzène-*p*-azobenzène („Cadion 2 B") et le benzène-diazoaminobenzène-*p*-azo-*p*-nitrobenzène („Cadion 3 B") qui donnent également des réactions d'adsorption avec Cd^{+2}, Mg^{+2} et Hg^{+2}. Le Cadion 2 B permettrait de détecter Cd^{+2} sur une goutte d'une solution à 0.16 μg Cd/ml.

Récemment RAZOUMOVA[13] a confirmé que la réaction Cadion–cadmium était bien une réaction d'adsorption.

TECHNIQUE PROPOSÉE

Appareillage

– Spectrophotomètre Jobin et Yvon, source: lampe à filament de tungstène l'étalonnage du monochromateur a été vérifié sur les raies 486.1 et 656.28 mμ de la lampe à hydrogène.

– Électrophotomètre Meunier.

Réactifs

a. *Réactifs purs pour analyse, Merck et Prolabo.*

b. *Solution de polyvinylpyrrolidone à 25% (Nom déposé Subtosan).*

c. *Réactif au Cadion.* Le réactif employé est le „Cadion" que l'on peut se procurer plus facilement que le „Cadion 2 B".

Le cadion commercial (Laboratoires du Bois de Boulogne) a été purifié par recristallisation dans l'alcool à 95° bouillant. Le produit obtenu après essorage et séchage fond à +198° (Bloc de Maquenne).

La stabilité du réactif a été étudiée en fonction des indications données par DWYER; une solution de cadion à 8 p.p.m. dans l'hydroxyde de potassium 0.2*N* et d'un degré alcoolique de 20° à 25° s'est montrée parfaitement stable dans le temps après étude spectrophotométrique.

On prépare comme suit la solution-mère de cadion à 0.02%:

Peser 20 mg de cadion, dissoudre dans l'hydroxyde de potassium alcoolique 0.02*N*, compléter à 100 ml. Filtrer sur verre fritté No. 4 après 24 h. Cette solution est d'une bonne conservation (garder le flacon bien bouché pour éviter l'action du CO_2 atmosphérique).

d. *Solution complexe.* La suite du travail nous a amenés à ajouter dans la solution finale 4‰ de tartrate de sodium et de potassium (pour empêcher la précipitation de certains hydroxydes métalliques) et 1‰ de polyvinylpyrrolidone comme colloide protecteur.

Ceci nous a conduits à utiliser, par commodité, la solution complexe suivante:

– Solution de cadion à 0.02%	10 ml
– Hydroxyde de potassium aq. 2*N*	25 ml
– Alcool à 95°	50 ml
– Solution de tartrate de potassium et de sodium à 20%	5 ml
– Solution de polyvinylpyrrolidone à 25%	1 ml
– Eau redistillée dans le verre q.s.p.	100 ml

Cette solution est préparée extemporanément pour chaque série de dosages.

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e. *Solution-mère de cadmium $10^{-3}M$ (soit 112.4 mg Cd au litre)*. Partir d'acétate neutre de cadmium pur pour analyse, ou de chlorure de cadmium pur pour analyse. Cette solution est stabilisée par addition de 5 ml/l d'acide chlorhydrique pur $10N$ redistillé dans le verre.

f. *Solution diluée de cadmium*. Au moment de l'emploi, préparer une solution aqueuse 1 ml = 2 µg Cd par dilution de la solution-mère de cadmium.

Mode opératoire

Dans une fiole jaugée* de 25 ml introduire 10 ml exactement mesurés de la solution complexe, puis la prise d'essai de cadmium à doser (en solution neutre, faiblement acide ou ammoniacale). Compléter au volume de 25 ml avec de l'eau redistillée. Établir dans les mêmes conditions une gamme-étalon de façon que le titre en Cd des solutions finales soit compris entre 0.05 et 0.6 p.p.m. Le témoin est préparé en mesurant 10 ml de solution complexe et en complétant au volume de 25 ml avec de l'eau redistillée.

Déterminer à l'aide d'un photomètre la différence des densités optiques du témoin et de chaque essai pour la longueur d'onde de 560 mµ et sous une épaisseur de 1 cm.

La présence de cadmium diminuant la densité optique, faire le zéro de l'appareil sur chaque essai, puis mesurer la densité optique du témoin.

La teneur en Cd de la prise d'essai est déduite de la courbe d'étalonnage établie. La Fig. 1 reproduit une courbe obtenue avec un spectrophotomètre à monochromateur et la Fig. 2 donne une courbe obtenue à l'aide d'un électrophotomètre Meunier (écran 57).

Nous avons observé l'importance de l'adsorption des ions Cd^{+2} à la surface des récipients en verre, phénomène longuement étudié par DWYER[14] en 1938. Cette particularité impose, en raison de la sensibilité de la réaction un lavage minutieux de toute la verrerie à l'aide d'un réactif capable d'arracher la totalité du cadmium adsorbé (solution de cyanure de potassium, ou ammoniaque diluée à 1 pour 5).

Ce dernier réactif est plus commode d'emploi et nous a donné satisfaction.

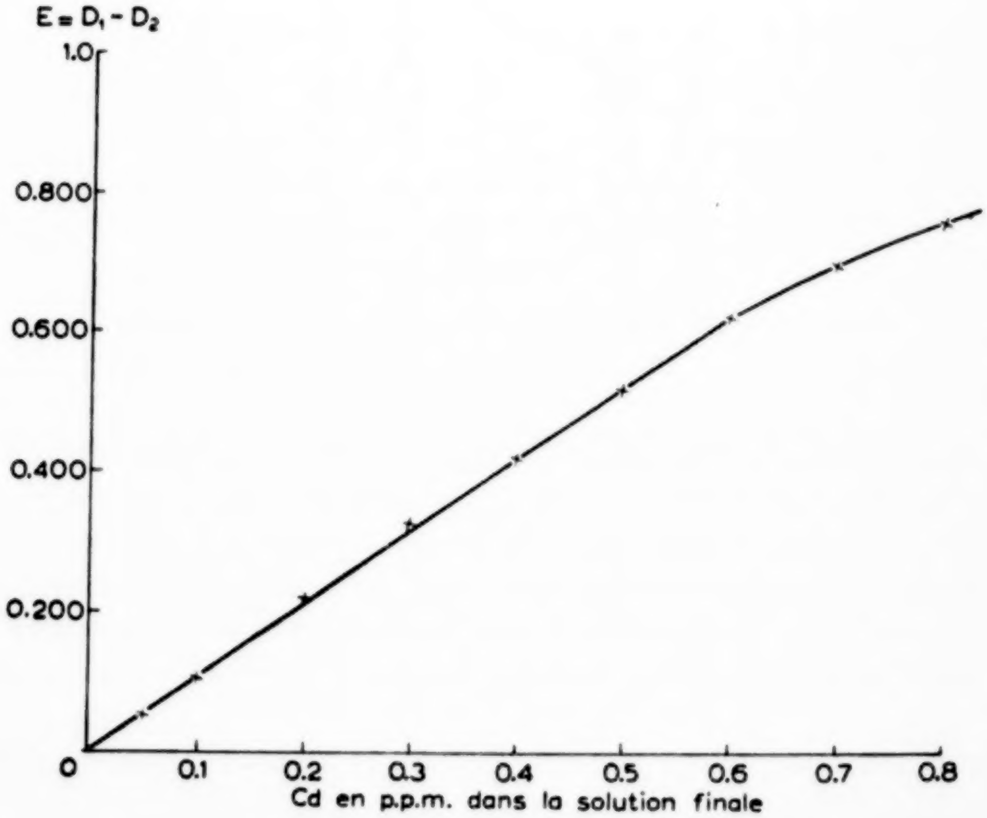

Fig. 1. Courbe d'étalonnage (Spectrophotomètre).

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* On peut évidemment utiliser des fioles jaugées de moindre capacité: 10, 5 ou 2 ml, en respectant les proportions relatives des réactifs, ce qui permet de pratiquer le dosage sur des prises d'essai de Cd plus faibles.

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DISCUSSION ET PARTIE EXPÉRIMENTALE

Spectres d'absorption

Les densités optiques expérimentales du réactif avec et sans cadmium ont été déterminées à l'aide du spectrophotomètre, pour les longueurs d'onde de 420 à 620 mμ; la pureté $\delta\lambda$ variait alors de 0.3 à 0.7 mμ. Les résultats sont indiqués dans la Fig. 3. Le réactif au cadion présente un maximum d'absorption à 555 mμ, en présence d'un excès de cadmium (2 à 10 p.p.m.) le maximum se déplace vers 475 mμ.

Il faut noter que le cadion en solution alcoolique et alcaline a un maximum d'absorption situé à 540 mμ, l'addition de polyvinylpyrrolidone au réactif déplace donc légèrement ce maximum vers le rouge.

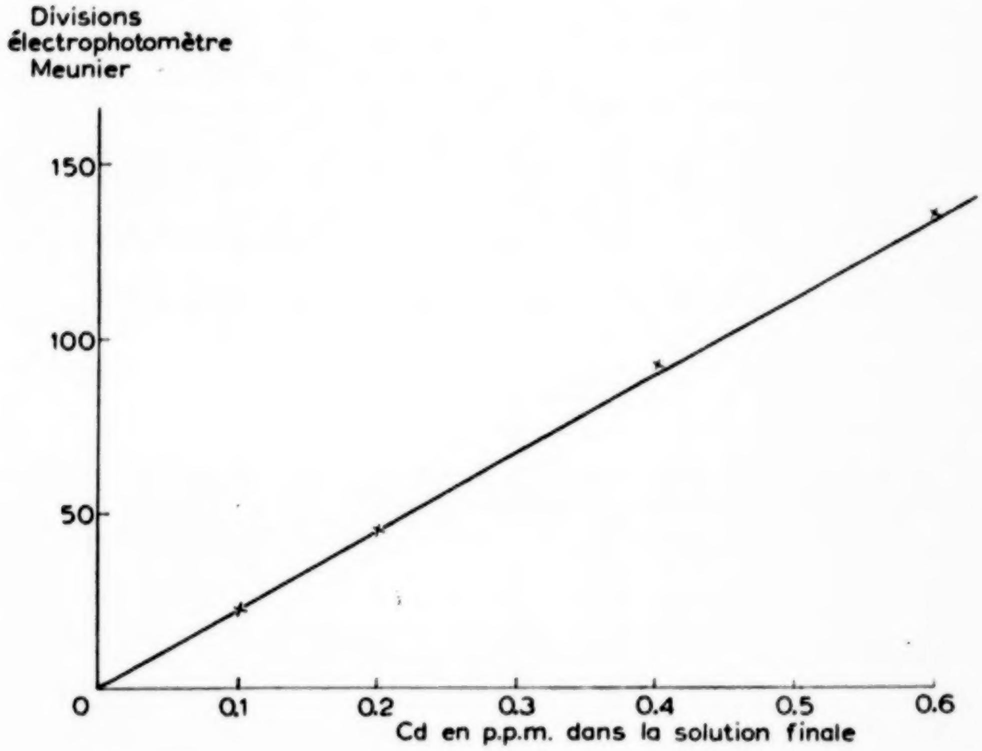

Fig. 2. Courbe d'étalonnage (Électrophotomètre Meunier).

L'étude des courbes d'absorption du réactif avec et sans cadmium montre que l'écart entre ces deux courbes est le plus grand vers 560 mμ, il nous a paru préférable d'utiliser cette longueur d'onde pour les mesures plutôt que la longueur d'onde du maximum d'absorption de la laque (475 mμ), ceci afin d'obtenir une plus grande sensibilité. Par ailleurs, l'utilisation d'une lumière verte est en général plus recommandable que l'utilisation d'une lumière bleue, si l'on se sert d'un photomètre à écrans.

La méthode consiste donc à mesurer l'excès de colorant restant après formation de la laque.

Influence du temps

Pour deux doses fixes de cadmium à la température de +20° on a étudié l'évolution de la réaction dans le temps.

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Nous voyons donc que dans les conditions expérimentales utilisées la réaction atteint rapidement son maximum, elle est stable suffisamment longtemps pour permettre les mesures.

Il faut noter que la polyvinylpyrrolidone paraît stabiliser la réaction qui, sans ce réactif, évolue très lentement sans se fixer parfaitement même après 60 min.

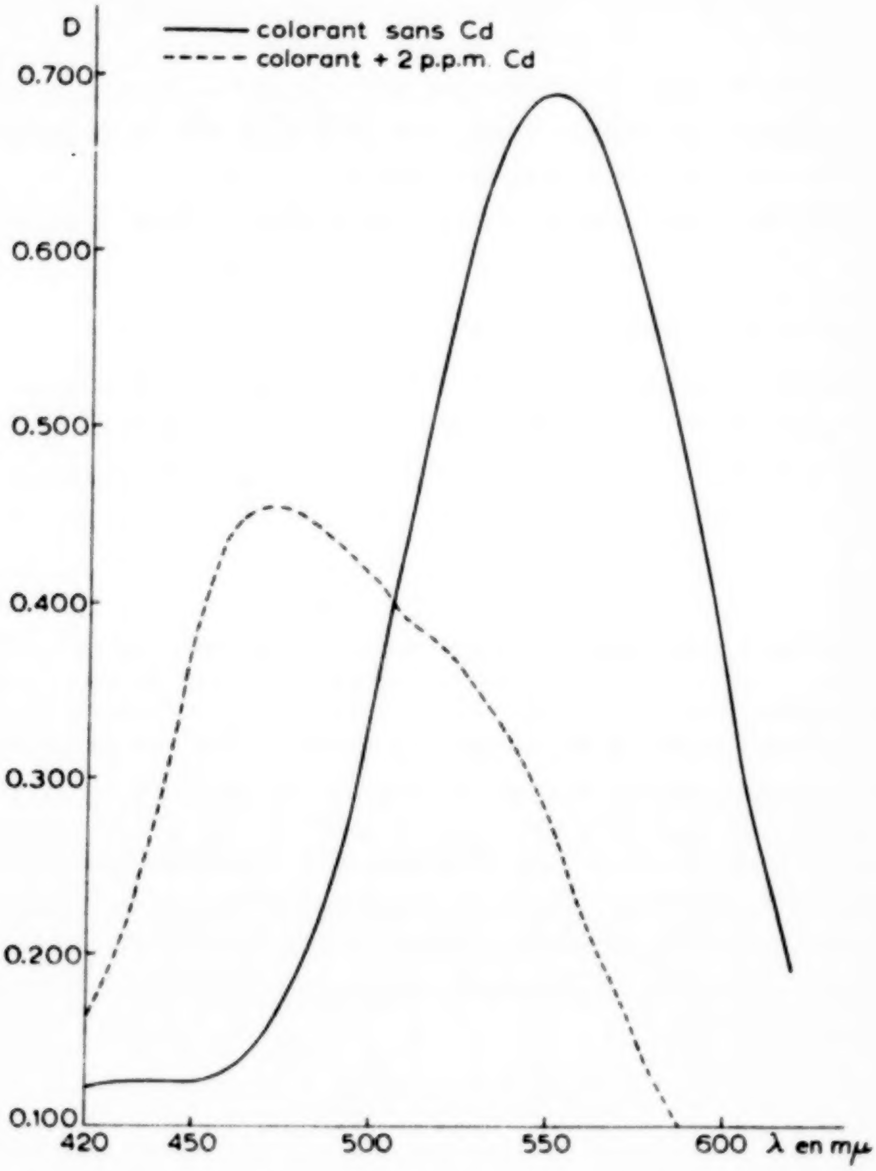

Fig. 3. Spectres d'absorption du réactif avec et sans cadmium.

TABLEAU I

Cd dans la solution finale	*Densités optiques après:* 5 min	10 min	15 min	30 min	60 min	120 min
0.1 p.p.m.	0.100	0.100	0.100	0.099	0.098	0.099
0.5 p.p.m.	0.515	0.515	0.515	0.515	0.515	0.515

Influence de la température

Pour deux doses fixes de cadmium on a laissé se développer la réaction pendant 10 min à des températures variables, les lectures ont été pratiquées après ce laps de temps.

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TABLEAU II

Cd dans la solution finale	*Densités optiques après 10 min à:* + 5°	+ 15°	+ 20°	+ 25°	+ 30°
0.1 p.p.m.	0.100	0.098	0.100	0.099	0.100
0.5 p.p.m.	0.520	0.510	0.515	0.510	0.515

On peut donc conclure que la réaction n'est influencée ni par le temps, ni par la température, les mesures pourront donc être pratiquées à la température du laboratoire et sans tenir compte d'un minutage précis.

Ajoutons que tous les essais ont été faits à la lumière solaire diffuse.

Influence des doses variables de cadmium

Ayant fixé la concentration en cadion à 8 p.p.m. pour des raisons de commodité de l'appareillage photométrique, nous avons étudié l'influence de doses variables de cadmium de 0 à 1 p.p.m. Les résultats obtenus sont objectivés dans le Tableau III et la Fig. 1.

TABLEAU III

Cd dans la solution finale en p.p.m.	*0.05*	*0.1*	*0.2*	*0.3*	*0.4*	*0.5*	*0.6*	*0.7*	*0.8*	*0.9*	*1*
Densité optique lue (Témoin-essai)	0.047	0.100	0.210	0.320	0.415	0.515	0.615	0.690	0.755	0.805	0.830

Il ressort de l'examen de la courbe obtenue que la loi de Beer est suivie entre 0 et 0.6 p.p.m.; au delà de cette concentration la courbe s'infléchit progressivement. La zone d'utilisation pratique se situe donc pour des doses de cadmium situées entre 0.05 et 0.5 p.p.m. La sensibilité de la méthode apparaît à la lecture des densités optiques obtenues.

TABLEAU IV

No. des essais	*Densité optique*	*Cd ajouté en p.p.m.*	*Cd trouvé en p.p.m.*
1	0.102	0.1	0.100
2	0.099	0.1	0.097
3	0.101	0.1	0.099
4	0.100	0.1	0.098
5	0.100	0.1	0.098
6	0.101	0.1	0.099
7	0.101	0.1	0.099
8	0.103	0.1	0.101
9	0.102	0.1	0.100
10	0.103	0.1	0.101

– Moyenne: 0.0992 p.p.m.
– Erreur quadratique moyenne: 0.0015 p.p.m. soit 1.5%

Étude de la reproductibilité et de l'exactitude du dosage

La courbe d'étalonnage précédente obtenue, afin d'étudier la reproductibilité et l'exactitude du dosage, nous avons pratiqué 10 dosages pour une quantité de 0.1 p.p.m. et 10 dosages pour une concentration de 0.5 p.p.m.

Les Tableaux IV et V explicitent les résultats.

TABLEAU V

No. des essais	*Densité optique*	*Cd ajouté en p.p.m.*	*Cd trouvé en p.p.m.*
1	0.520	0.5	0.500
2	0.525	0.5	0.505
3	0.520	0.5	0.500
4	0.520	0.5	0.500
5	0.520	0.5	0.500
6	0.525	0.5	0.505
7	0.520	0.5	0.500
8	0.525	0.5	0.505
9	0.520	0.5	0.500
10	0.525	0.5	0.505

- Moyenne: 0.502 p.p.m.
- Erreur quadratique moyenne: 0.003 p.p.m. soit 0.6%.

Essai d'étude théorique

Ce travail avait pour but d'essayer de savoir dans quelle proportion moléculaire le cadmium et le cadion réagissent pour former le complexe étudié.

A cet effet il a été préparé une solution $10^{-3}M$ de cadion, soit 346 mg au litre, dans les conditions précisées précédemment; toutefois le tartrate de sodium et de potassium n'a pas été ajouté.

1°. *Influence de doses croissantes de colorant sur une dose fixe de cadmium.* Pour une concentration fixe en cadmium de $4 \cdot 10^{-6}M$, la teneur en colorant variait de $2 \cdot 10^{-6}M$ à $48 \cdot 10^{-6}M$. La Fig. 4 représente les densités optiques lues à 560 mμ.

2°. *Influence de doses croissantes de cadmium sur une dose fixe de colorant.* Pour une concentration fixe en colorant de $24 \cdot 10^{-6}M$, la teneur en cadmium variait de $2 \cdot 10^{-6}M$ à $40 \cdot 10^{-6}M$. Les résultats obtenus sont représentés dans la Fig. 5.

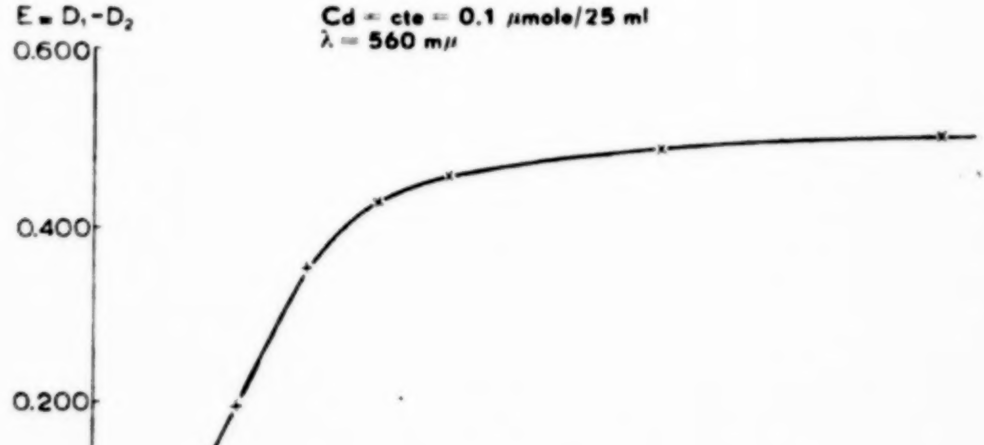

Fig. 4. Influence de doses croissantes de colorant sur une dose fixe de cadmium.

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3°. *Méthode des variations continues.* La méthode de JOB des variations continues[15] a été appliquée en ajoutant X ml d'une solution $10^{-4}M$ de colorant à (10—X) ml d'une solution équimoléculaire de cadmium et en complétant au volume de 25 ml.

Pour chaque mesure le témoin était constitué par une solution à même concentration en réactifs mais exempte de cadmium.

Les densités optiques lues sont indiquées dans la Fig. 6.

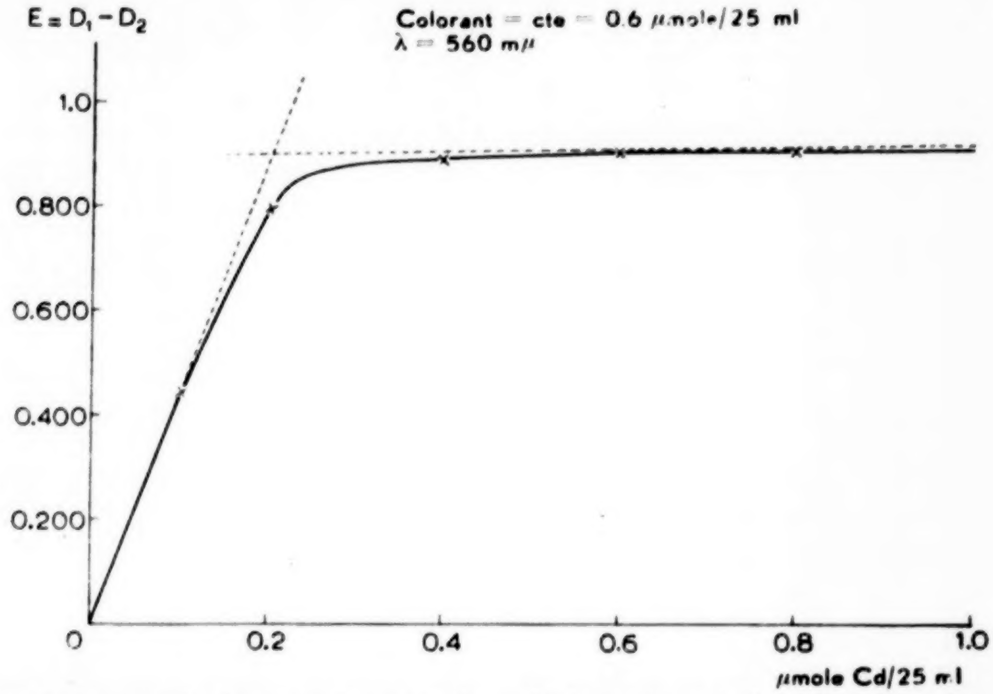

Fig. 5. Influence de doses croissantes de cadmium sur une dose fixe de colorant.

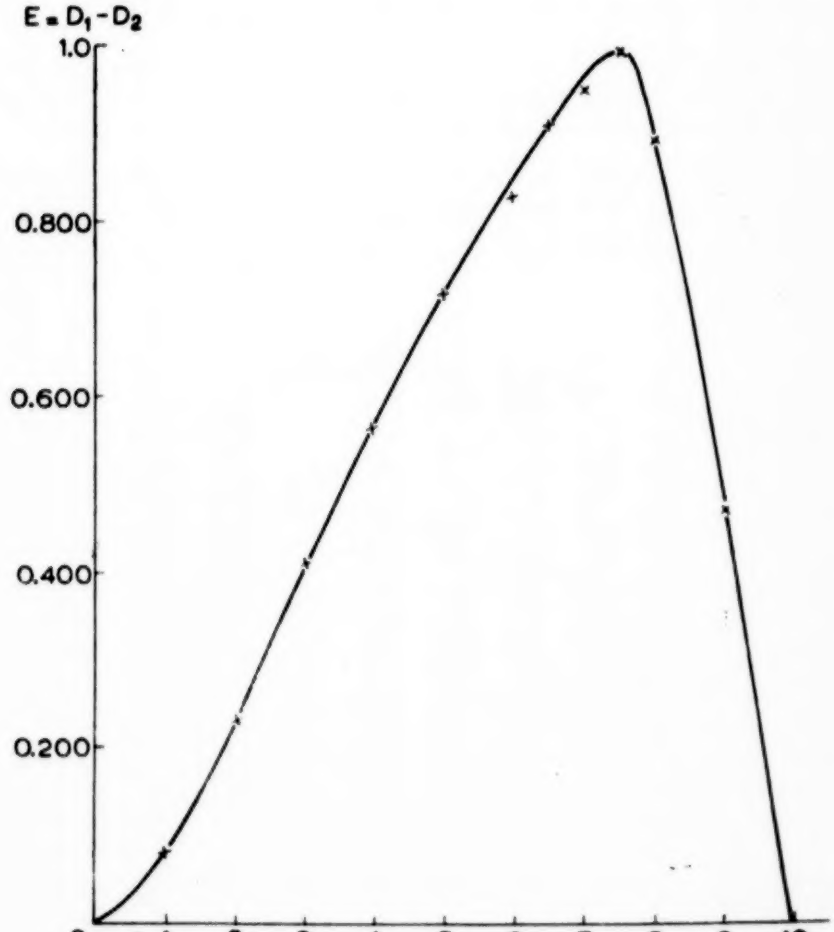

Fig. 6. Méthode des variations continues.

La densité optique maximum obtenue était trouvée pour le rapport

$$\frac{7.5 \text{ Colorant}}{2.5 \text{ Cd}} \quad \text{soit} \quad \frac{3 \text{ Colorant}}{1 \text{ Cd}}$$

Ce rapport, est également celui qui est indiqué par la courbe de la Fig. 5 (colorant = constante). Par contre, la courbe de la Fig. 4 (Cd = constante) fournit un rapport voisin de $\frac{4 \text{ Colorant}}{1 \text{ Cd}}$. Ce fait pourrait s'expliquer par une différence dans la dissociation du complexe.

Il semble donc que, dans les conditions expérimentales utilisées, le rapport $\frac{\text{Colorant}}{\text{Cd}}$ soit de $\frac{3}{1}$.

Étude des ions étrangers

L'influence des ions les plus courants sur le dosage du cadmium a été examinée.

L'étude a été pratiquée à l'aide d'un électro-photomètre Meunier sur 37 ions, dont 18 anions et 19 cations pour une quantité de 0.5 p.p.m. de Cd, le rapport $\frac{\text{ion étranger}}{\text{Cd}}$ était de 10, 100 et 1000 pour les anions et de 1, 5, 10 et 100 pour les cations.

Les résultats sont reproduits dans les Tableaux VI et VII.

TABLEAU VI

Nature de l'ion	*Sel utilisé*	*Rapport* $\frac{\textit{ion étranger}}{\textit{Cd}}$	*Cd ajouté en p.p.m.*	*Cd trouvé en p.p.m.*
F^-	NaF	1.000	0.5	0.490
Cl^-	KCl	1.000	0.5	0.490
Br^-	KBr	1.000	0.5	0.505
I^-	KI	1.000	0.5	0.495
BO_2^-	$B(OH)_3$	1.000	0.5	0.500
CO_3^{-2}	K_2CO_3	1.000	0.5	0.495
$H_2PO_4^-$	KH_2PO_4	1.000	0.5	0.500
NO_3^-	KNO_3	1.000	0.5	0.490
NO_2^-	KNO_2	1.000	0.5	0.490
SO_4^{-2}	K_2SO_4	1.000	0.5	0.500
$HAsO_4^{-2}$	Na_2HAsO_4	1.000	0.5	0.505
AsO_2^-	As_2O_3	10	0.5	0.485
		100	0.5	0.480
		1.000	0.5	0.470
ClO_3^-	$KClO_3$	1.000	0.5	0.500
CrO_4^{-2}	K_2CrO_4	100	0.5	0.495
		1.000	0.5	0.475
CN^-	KCN	5	0.5	0.495
		10	0.5	0.480
		100	0.5	0.160
		1.000	0.5	0
CH_3COO^-	$NaOOCCH_3$	1.000	0.5	0.505
Oxalate	$(COOH)_2$	1.000	0.5	0.500
Citrate	Na Citrate	1.000	0.5	0.495

Parmi les anions examinés et aux erreurs d'expérience près, on voit que seul CN^- interfère dans le dosage du cadmium.

Les cations étrangers étudiés peuvent se diviser en trois groupes:

1) Ceux qui ne gênent pas le dosage aux concentrations essayées (Alcalins Zn^{+2}, Pb^{+2}, Bi^{+3}, Al^{+3}, Sb^{+3});

TABLEAU VII

Nature de l'ion	*Sel utilisé*	*Rapport* $\frac{\text{ion étranger}}{\text{Cd}}$	*Cd ajouté en p.p.m.*	*Cd trouvé en p.p.m.*	
				Directement	*Incréments*
NH_4^+	NH_4Cl	1.000	0.500	0.500	
Li^+	$LiCl$	100	0.500	0.500	
Na^+	$NaCl$	1.000	0.500	0.490	
Mg^{+2}	$MgCl_2$	1	0.500	0.475	
		5	0.500	0.430	0.500
		10	0.500	0.340	
		100	0.500	trouble	
Ca^{+2}	$CaCl_2$	5	0.500	0.500	
		10	0.500	0.430	
		100	0.500	0	
Mn^{+2}	$MnCl_2$	5	0.500	0.500	
		10	0.500	0.475	
		100	0.500	précipité	
Fe^{+3}	$FeCl_3$	1	0.500	0.495	
		5	0.500	0.470	
		10	0.500	0.430	0.495
		100	0.500	0.100	
Co^{+2}	$CoCl_2$	1	0.500	0.485	
		5	0.500	0.465	
		10	0.500	0.400	
		100	0.500	0.300	
Ni^{+2}	$NiSO_4$	1	0.500	0.490	
		5	0.500	0.470	
		10	0.500	0.430	
		100	0.500	0.420	
Cu^{+2}	$Cu(NO_3)_2$	1	0.500	0.505	
		5	0.500	0.475	
		10	0.500	0.460	
		100	0.500	0.370	0.490
Ag^+	$AgNO_3$	1	0.500	×	
Zn^{+2}	$ZnSO_4$	100	0.500	0.500	
Hg^{+2}	$HgCl_2$	1	0.500	×	
Tl^+	Tl_2SO_4	10	0.500	0.490	
		100	0.500	0.485	
Sn^{+2}	$SnCl_2$	1	0.500	0.485	
		5	0.500	0.450	
		10	0.500	0.410	
		100	0.500	0.300	
Pb^{+2}	$Pb(CH_3COO)_2$	100	0.500	0.500	
Sb^{+3}	Emétique	100	0.500	0.500	
Bi^{+3}	$Bi(NO_3)_3$	100	0.500	0.500	
Al^{+3}	$Al_2(SO_4)_3$	100	0.500	0.495	

2) Ceux qui donnent une réaction voisine de celle du cadmium: Hg^{+2} et Ag^+ qui doivent obligatoirement être séparés avant le dosage. Cette séparation se pratique facilement par réduction de Hg^{+2} et de Ag^+ à l'état métallique à l'aide de l'hydroxylamine en milieu ammoniacal.

Le cadmium reste en solution à l'état de complexe aminé; après centrifugation on prélève une partie aliquote et procède au dosage. On a pu ainsi doser exactement 0.5 p.p.m. de Cd^{+2} en présence de 100 fois de Hg^{+2} et de 100 fois de Ag^+.

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3) Le plus grand nombre des autres cations désensibilisent plus ou moins la réaction Cd–cadion. Il convient dans ce cas de séparer l'ion ou les ions gênants par les méthodes classiques. (Un exemple de séparation de Ca^{+2} à l'occasion de l'application aux eaux potables, et des exemples de séparation grossière du cadmium au milieu d'autres ions par la méthode à la dithizone, seront fournis ci-dessous); toutefois dans de nombreux cas, la loi de Beer reste valable et la méthode des incréments[16] permet d'effectuer le dosage sans séparation.

Le Tableau VII (dernière colonne à droite) donne quelques exemples des résultats obtenus avec Mg^{+2}, Fe^{+3}, et Cu^{+2}.

APPLICATION DE LA MÉTHODE PROPOSÉE À QUELQUES CAS PARTICULIERS

Microdosage du cadmium dans une eau

L'eau de Paris (terneur en calcium de l'ordre de 100 mg/l) a été utilisée pour les essais.

Le calcium doit, être éliminé à l'état d'oxalate pour permettre le dosage.

Technique

Fiole jaugée de 25 ml	Solution complexe	10 ml
	Solution d'acide oxalique à 1%	1 ml
	Eau essayée	10 ml
	Eau redistillée	q.s.volume

Mélanger, laisser précipiter pendant 2 h, centrifuger, mesurer la densité optique du liquide. On peut se reporter à la courbe d'étalonnage en solution pure, soit (cas plus général) utiliser la méthode des incréments.

Exemples de résultats obtenus

	Cadmium ajouté µg	*Cadmium trouvé* µg
10 ml d'eau de Paris	0	0
	1.25	1.0
	2.5	2.3
	5	5
	7.5	7.6

Microdosage du cadmium en présence de grandes quantités d'autres métaux

Lorsque les cations gênants sont en trop grande quantité, il faut procéder à une séparation préalable grossière du cadmium, nous entendons par là que cette séparation doit conduire à une solution contenant tout le cadmium de la prise d'essai et les autres métaux en quantités ne pouvant pas gêner la réaction.

Une méthode classique de ce type utilise la formation de dithizonates. Nous donnons ci-dessous la technique que nous avons employée, empruntée à la première partie du travail de SALTZMAN[3]. La séparation est basée sur l'emploi d'une extraction chloroformique du dithizonate de cadmium en milieu fortement alcalin et en présence de complexants (cyanure, tartrate).

Introduire dans une ampoule à décantation les réactifs suivants, dans l'ordre, et en agitant chaque fois:

– Solution de cadmium à doser (10 µg de Cd par exemple)	
– Eau redistillée dans le verre	20 ml
– Solution aqueuse de tartrate de sodium et de potassium à 20% (p/vol.)	2 ml
– Solution aqueuse à 40% de NaOH et 1% de KCN	8 ml
– Solution chloroformique de dithizone purifiée à 30 mg/l.	20 ml

Agiter fortement et séparer rapidement la couche chloroformique dans une deuxième ampoule à décantation contenant 10 ml d'HCl 0.1*N*. Extraire à nouveau deux fois avec 10 ml de chloroforme, joindre les deux extraits chloroformiques au premier.

Agiter la deuxième ampoule à décantation afin de faire passer le cadmium en phase aqueuse acide.

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Séparer cette dernière, laver le chloroforme et l'ampoule à décantation deux fois à l'eau redistillée; la solution ainsi obtenue sert au dosage par le cadion.

On a trouvé ainsi:

1er essai : 9.6 μg Cd pour 10 μg
2ème essai : 9.9 μg Cd pour 10 μg

L'extraction pratiquée est donc totale: Si l'on opère en présence de métaux qui gênent le dosage direct du cadmium, on extrait, outre le dithizonate de cadmium, partiellement d'autres dithizonates métalliques (Pb et Zn en particulier) mais cela ne gêne pas le dosage final.

1er exemple. Solution contenant: 5 mg Cu^{+2}, 5 mg Fe^{+3}, 5 mg Zn^{+2}, 5 mg Pb^{+2}, 5 mg Co^{+2}, 5 mg Mg^{+2}, 5 mg Ca^{+2}, 10 μg Cd^{+2}.

Trouvé: 9.6 μg Cd.

2ème exemple. La même technique a été employée mais en remplaçant les 10 ml d'HCl 0.1 *N* pour décomposer les dithizonates extraits par 10 ml de solution aqueuse d'acide citrique à 1%.

En présence du même mélange complexe que ci-dessus, il a été trouvé 9.85 μg pour 10 μg introduits.

Ainsi, en alliant la méthode classique d'extraction à la dithizone à la précision et à la meilleure spécificité de la méthode au cadion, la technique proposée peut être appliquée dans des milieux particulièrement complexes.

RÉSUMÉ

Il est proposé une nouvelle méthode de microdosage spectrophotométrique du cadmium utilisant un colorant triazène, le "Cadion".

La méthode est très sensible et permet de doser 0.05 p.p.m. de cadmium dans la solution finale, la reproductibilité et la précision sont satisfaisantes.

Une étude de l'interférence des principaux anions et cations étrangers est pratiquée; l'élimination des ions gênants est indiquée.

Enfin, quelques exemples d'application de la méthode proposée, sont donnés.

SUMMARY

A new method is presented for spectrophotometric micro-determinations of cadmium by means of a triazine dye, called "Cadion".

The method is a highly sensitive one, permitting the determination of 0.05 p.p.m. cadmium in the final solution, with satisfactory accuracy and reproducibility.

The interference of the main foreign anions and cations is studied, and a way of eliminating the interfering ions is suggested.

Some examples are given for the application of the proposed method.

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Reçu le 24 janvier 1958

DETERMINATION OF COPPER, LEAD, TIN AND ANTIMONY BY CONTROLLED-POTENTIAL ELECTROLYSIS

II. APPLICATION OF THE METHOD TO THE DETERMINATION OF Cu, Pb, Sn, AND Sb IN BRONZES AND BRASSES

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BRIEF SURVEY OF THE PREVIOUSLY DEVELOPED ELECTROLYTIC METHODS

The classic methods of determining copper, lead, tin and antimony in copper-base alloys and particularly in bronzes are based on nitric acid dissolution and on rendering tin and antimony insoluble. From the nitric solution copper and lead are separated electrolytically: copper at the cathode as pure metal, and lead at the anode as dioxide. The use of sulfamic acid inhibits both the depolarizing action of nitrous vapours[1,2] and the anodic deposition of manganese as dioxide[3]. However, the need to recover the copper coprecipitated with metastannic acid has prompted many analysts to study other methods whose main principle is that the alloy to be analysed is first completely dissolved ; this is achieved by the use of nitric acid to which hydrofluoric[4], phosphoric[5] or perchloric[6] acid has been added; more recently, a mixture of hydrofluoric and boric acids[7,8] has been used with advantage. All the above methods, however, permit the electrolytical determination only of copper and lead.

The only acid that by itself is capable of completely dissolving the alloys of these metals is hydrochloric acid; from the solution obtained, all the four elements under examination may be deposited, provided the cathode potential is suitably adjusted and provided the evolution of chlorine is checked by an anodic depolarizer. Growing attention is being paid by analysts to this technique, especially after the development of adequate electronic equipment which permits the automatic control of the cathode potential[9-28]; however, even an analysis carried out with manually controlled equipment[28] is often superior to the usual methods.

In a hydrochloric solution, copper and tervalent antimony are deposited practically at the same cathode potential (—0.35 V *vs.* S.C.E.); at more negative potential (—0.6 to —0.7 V *vs.* S.C.E.) lead and tin are deposited together. A first practical set-up based on these methods was employed by LASSIEUR[29] and DIEHL[9]: copper and antimony are deposited simultaneously, the deposit is then re-dissolved and copper alone deposited from a nitric-hydrofluoric acid solution. Lead and tin are separated simultaneously from the electrolyte remaining after removal of copper and antimony. This deposit is also re-dissolved and, subsequently, lead and tin are deposited, the former in hydrofluoric medium and the latter in oxalic medium.

A not very different micro-analytical technique has been developed by LINDSEY AND TUCKER[30]. LINGANE AND JONES[12,14,28] have shown that copper, bismuth and lead can be successively separated from hydrochloric-tartaric solutions brought to a very slightly acid pH by sodium hydroxide. They also showed that by acidifying the residual solution with hydrochloric acid, tin also may be separated.

LINGANE AND JONES have systematically investigated the influence of pH, of tartrates, of temperature, the action of anodic depolarizers and the copper-deposition mechanism. Although their method also permits bismuth to be deposited separately, it is, however, disturbed by the presence of antimony and nickel which partially co-deposit with tin. Furthermore, a lead loss occurs during washing, which loss the authors computed to be 1.5 ± 0.6 mg.

AYLWARD AND BRYSON[31] dissolved the sample in hydrochloric and nitric acid and then eliminated these acids by phosphoric acid. From the phosphoric solution, first the copper and then the lead were separated; to avoid lead losses during washing, on completion of lead electrolysis these authors neutralized the solution with ammonia and washed the deposit first with a dilute ammonium sulphate solution, then with distilled water. Tin was determined volumetrically. Antimony causes disturbances because most of it deposits with the lead; bismuth deposits before all the copper has been deposited; furthermore, not more than 450 mg of copper must be present.

Copper deposition from hydrochloric acid solutions in the presence of lead, tin and antimony, has been the object of many researches. DIEHL AND BROUNS[32,9] demonstrated that in a 1N HCl solution the cupric ion Cu^{+2} is reduced first to the chlorocuprous complex $CuCl_3^{-2}$ and then to the metal. The $CuCl_3^{-2}$ ion formed at the cathode is oxidised to cupric ion at the anode; furthermore, the cathode deposit may be reoxidised by the cupric ion:

$$Cu + Cu^{+2} + 6Cl^- \rightarrow 2CuCl_3^{-2}$$

Besides the use of hydroxylamine as anodic depolarizer, DIEHL AND BROUNS recommended the addition of some stannous chloride (if tin is not already present in the solution) to reduce the copper to the cuprous state.

According to LINGANE[13], these difficulties may be overcome by keeping the hydrochloric acid concentration below 0.5N and by using hydrazine as depolarizer instead of the less effective hydroxylamine.

FOSTER[33] used up to 4 g of hydrazine dihydrochloride when the amount of copper present was more than 800 mg. However, he points out that in some cases he has had to wait for more than one hour before copper started to deposit in appreciable amounts. He then used a porous cylinder to isolate the anode[34], thus succeeding in reducing the duration of electrolysis by approximately 50%. After depositing the copper, FOSTER deposited the lead and tin according to LINGANE AND JONES' method, and then the zinc from an ammonia solution. The presence of antimony and nickel was not taken into account. Iron must be absent if zinc is to be deposited.

ANALYSIS OF BRONZES AND BRASSES BY A NEW METHOD

In a previous paper[35], a method has been described for the successive deposition of copper, lead, tin and antimony. Arsenic and bismuth were not considered in that method, since the alloys analysed in this laboratory do not contain these elements or, if they do, in trace amounts only. The method[35] is similar to that of LINGANE AND JONES[14,28] since a tartaric medium is utilized for copper and lead determination and an acid (hydrochloric acid) medium for tin determination. Not only does antimony not interfere, but it may even be determined after the tin.

The method outlined in the above-mentioned paper[35] is applied here for the determination of Cu, Pb, Sn and Sb in copper-base alloys in which tin and zinc are the main alloying elements. Though the nomenclature of these alloys is not clearly distinctive (*cf.* for instance the manganese bronzes in which the amount of tin is practically nil), here the tin alloys are designated as bronzes and the zinc alloys as brasses.

The following additional hints are given to complete the instructions outlined in the description of the general method of analysis[35].

(a) Bronzes

The solution may contain up to 0.9 g of Cu in the presence of: Pb (from 2 to 120 mg), Sn (from 4 to at least 200 mg) and Sb (from 1.5 to 15 mg); at least 100 mg of each of the following elements may also be present Ni, Zn and Mn, and at least 50 mg of Fe. P and S may also be present in the alloy sample. Al may be present in amounts up to 10 mg. Higher proportions of Al interfere with the electrolysis of Pb because, most probably, the greater the amount of aluminium present, the

TABLE 1

ANALYSIS OF BRONZE-TYPE ALLOYS (1-g samples)

Sample	*No.*	*Results*			
		Cu	*Pb*	*Sn*	*Sb*
N. 207 Bronze C (B.Ch.S.)	1	86.60	0.38	9.80	n.d.
Cu = 86.65 – 87; Sb = 0.04; Fe = 0.06					
S = 0.055	2	86.76	0.36	9.87	n.d.
Pb = 0.41; Ni = 0.09; As = 0.05;					
P = 0.055	3	86.82	0.37	9.86	n.d.
Sn = 9.71 – 9.97; Zn = 2.53; Ag = 0.02	4	86.80	0.38	9.87	n.d.
N. 124 c Ounce Metal (N.B.S.)					
Cu = 84.22; Zn = 4.93; S = 0.048	1	84.15	4.71	5.13	0.21
Pb = 4.74; Ni = 0.60; P = 0.024	2	84.14	4.68	5.12	0.16
Sn = 5.13; Fe = 0.107					
Sb = 0.20; Si = 0.002					
N. 63 c Phosphor Bronze (N.B.S.)	1	80.51	9.33	8.95	0.50
Cu = 80.46; Ni = 0.32; As = 0.02	2	80.50	9.37	8.97	0.48
Pb = 9.35; P = 0.15; Fe = 0.002	3	80.45	9.40	8.98	0.50
Sn = 9.03; Zn = 0.09	4	80.46	9.30	8.96	0.47
Sb = 0.52; S = 0.06	5	80.49	9.31	8.94	0.49
N. 63 b Phosphor Bronze (N.B.S.)	1	77.90	9.32	9.68	0.48
Cu = 77.94; Zn = 0.71; P = 0.44	2	77.88	9.33	9.72	0.51
Pb = 9.36; Fe = 0.47; S = 0.16	3	77.86	9.30	9.72	0.52
Sn = 9.78; Ni = 0.33; Ag = 0.04	4	77.87	9.35	9.71	0.49
Sb = 0.54; Si = 0.12; Al = 0.05	5	77.84	9.37	9.74	0.48
N. 52 c Cast Bronze (N.B.S.)					
Cu = 89.25; Zn = 2.12; S = 0.002	1	89.28	n.d.	7.83	—
Pb = 0.011; Ni = 0.76; P = 0.001	2	89.25	n.d.	7.77	—
Sn = 7.85; Fe = 0.004					
N. 158 Silicon Bronze (N.B.S.)					
Cu = 90.86; Si = 2.72; Mn = 1.31	1	90.77	n.d.	0.92	—
Pb = 0.004; Zn = 2.07; Al = 0.54	2	90.90	n.d.	0.88	—
Sn = 0.97; Fe = 1.48; Ni = 0.006					

more negative must the cathode potential be at which Pb is deposited. No other precautions are required for the analysis of these alloys. Table I shows the results obtained in analysing bronzes of known composition: the analysis values found are in strict agreement with those certified by N.B.S.

(b) *Brasses*

Copper electrolysis is carried out as described in the general method. Lead deposition is started at —0.60 V *vs.* S.C.E., then descending gradually to —0.70 V *vs.* S.C.E.

Zinc in amounts up to 450 mg does not cause disturbance (Table III, No. 2). Aluminium does not disturb copper deposition and — up to 60 mg — not even lead deposition (Table II); in the presence of 100–120 mg of aluminium lead deposits from —0.70 to —0.75 V *vs.* S.C.E. (Table II, No. 2) The method also yields good results in the case of low Pb and Sn percentages, as evidenced in Table II; see also Table III.

TABLE II

ANALYSIS OF BRASS TYPE ALLOYS (1-g samples)

Sample	*No.*	*Results*			
		Cu	*Pb*	*Sn*	*Sb*
N. 62 b Manganese Bronze (N.B.S.)					
Cu = 57.39; Zn = 37.97; Ni = 0.27	1	57.44	0.19	0.92	n.d.
Pb = 0.28; Mn = 1.29; Si = 0.048	2	57.45	0.30	0.97	n.d.
Sn = 0.96; Al = 0.97; As = 0.004	3	57.41	0.26	0.92	n.d.
Sb = 0.005; Fe = 0.82; Ag = 0.005	4	57.42	0.22	0.92	n.d.
N. 62 c Manganese Bronze (N.B.S.)					
Cu = 59.16; Zn = 37.24; Mn = 0.66	1	59.16	0.20	0.35	—
Pb = 0.24; Al = 1.22; Ni = 0.28	2	59.19	0.20	0.41	—
Sn = 0.39; Fe = 0.74; Si = 0.068					
N. 37 d Sheet Brass (N.B.S.)					
Cu = 70.78; Sn = 0.97; Ni = 0.58	1	70.78	0.92	0.93	—
Pb = 0.94; Zn = 26.65; Fe = 0.076	2	70.80	0.98	0.93	—
N. 164 Manganese – Aluminium Bronze (N.B.S.)					
Cu = 63.76; Zn = 21.89; Fe = 2.52	1	63.67	0.20	0.67	—
Pb = 0.22; Al = 6.21; Ni = 0.046	2[a]	63.74	0.16	0.59	—
Sn = 0.63; Mn = 4.68; Si = 0.038	3[b]	63.74	0.19	0.66	—

[a] To the sample of test No. 2, 0.05 g of nickel as chloride was added; lead was deposited at —0.70 to —0.75 V *vs.* S.C.E.

[b] To the sample of test No. 3, 0.04 g of aluminium as metal and 0.05 g of nickel as chloride were added; lead was deposited at —0.70 to —0.75 V *vs.* S.C.E.

(c) *Presence of silicon*

For bronzes and brasses containing silicon, dissolution in a flask provided with a condenser, as described in the general method is particularly suitable; after adding tartaric acid, filter off the residue, collect the filtrate in a tall-form 400-ml beaker and then proceed according to the general method. Often the residue is dark, probably because it also contains silicides, principally of iron, manganese and nickel. Silicon is partially soluble in the copper matrix, but it also combines with some alloying elements to form silicides that precipitate and remain dispersed in extremely fine particles. The acid dissolution of the alloy leaves the silicides practically unaffected. In the samples examined, spectrographic analysis of the residue has shown that copper, lead and tin (no antimony was present) pass quantitatively into the filtrate. In Table I the analysis of a silicon bronze is given.

(d) *Precautions for the analysis of a 2-g sample*

Generally a 1-g alloy sample is sufficient for the analysis. However, when lead and tin percentages are low, the determination may be carried out on a 2-g sample. Dissolve with 15 ml of diluted HCl and H_2O_2. After the dissolution is complete, add another 5 ml of diluted HCl and then proceed as usual.

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TABLE III

ANALYSIS ON 2-g SAMPLES

Sample	*No.*	*Results*		
		Cu	*Pb*	*Sn*
1) N. 207 Bronze C				
Cu = 86.65—87; Zn = 2.53; Ag = 0.02	1	86.76	0.44	9.80
Pb = 0.41; Ni = 0.09; S = 0.055	2	86.72	0.41	9.84
Sn = 9.71—9.97; Fe = 0.06; P = 0.055	3	86.66	0.40	9.82
Sb = 0.04; As = 0.05	4	86.74	0.41	9.83
		a		
2) N. 164 Manganese–Aluminium Bronze				
Cu = 63.76; Zn = 21.89; Fe = 2.52	1	63.73	0.18	0.65
Pb = 0.22; Al = 6.21; Ni = 0.046	2	63.74	0.25	0.60
Sn = 0.63; Mn = 4.68; Si = 0.038		b	b	
3) N. 62 b Manganese Bronze N. 62 c Manganese Bronze N. 37 d Sheet Brass (Composition: see Table II)	The analysis on 2-g samples cannot be carried out, since a zinc salt precipitates during copper electrolysis.			

[a] Ammonia was added during copper electrolysis because the buffer capacity of the solution was insufficient to keep the pH unchanged.

[b] Copper deposition was regular; lead deposited at —0.70 to —0.75 V *vs.* S.C.E. (over 120 mg of aluminium were present).

The addition of ammonia up to a pH = 5, however, is often apt to cause partial precipitation of copper, possibly as a tartrate or a succinate; during copper electrolysis, this precipitate often clings to the cathode, without, however, doing any harm, since the precipitate dissolves as the electrolysis progresses. The addition of ammonia may also be limited to the amount giving a pH not higher than 4; in this case, the buffer capacity of the solution may be insufficient to keep the pH constant. Therefore, during electrolysis, check the pH occasionally with narrow-range pH test papers and when it drops below 3.5, restore to 4.5–5 by additions of small quantities of ammonia.

Lead and tin electrolysis proceed regularly.

The possibility of working with 2-g samples is limited by zinc which, if present in amounts greater than 450–500 mg, precipitates during copper electrolysis (Table III, No. 3).

Table III shows the results of some analyses carried out on 2-g samples: the results substantially agree with those obtained with 1-g samples, but results were better with bronze C 207 as regards lead.

SUMMARY

A brief survey is given of electrolytic methods for determining some constituents in bronzes and brasses. Then a report is presented of the application of a new controlled potential electrolytic method, described in a previous paper, to the determination of Cu, Pb, Sn and Sb in the above mentioned materials.

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Received February 25th, 1958

COULOMETRIC TITRATION OF GOLD WITH ELECTROGENERATED CHLORO-CUPROUS ION

by

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This communication describes a method for the coulometric titration of +3 gold with electrogenerated +1 copper in a hydrochloric acid medium, the net titration reaction being

$$AuCl_4^- + 3CuCl_2^- \rightarrow Au + 3Cu^{+2} + 10Cl^- \quad \ldots\ldots \quad (1)$$

Although the coulometric titration technique has been applied very extensively[1], its application to the determination of gold has not previously been reported.

The aqueous solution chemistry of gold is not amenable to much variety of titrimetric determination. Because most aurous compounds readily disproportionate into corresponding auric compounds and the metal, the sample solution almost invariably will contain the gold in the +3 state. Except for POLLARD's iodometric method[2], most of the few extant methods for the titration of gold are based on reduction from the +3 state to the metal, employing such reductants as ferrous ion, titanous ion, chromous ion, and hydroquinone[3]. The use of dichloro cuprous ion as reductant does not seem to have been previously suggested. Being a somewhat stronger reductant (in hydrochloric acid medium) than ferrous iron and hydroquinone it produces a greater rate of change of equilibrium balance of the titration reaction at the equivalence point, and since it is a weaker reductant than titanous ion it is easier to generate with 100% current efficiency. It has previously been employed very successfully by MEIER, MEYERS AND SWIFT[4] for the coulometric titration of dichromate ion and vanadate ion.

EXPERIMENTAL TECHNIQUE

Fig. 1 shows the titration cell, whose capacity is *ca.* 100 ml. The generator cathode is pure gold wire (1.5 mm diam.) coiled in the form of a flat spiral with an area of 14 cm^2. This electrode shape, and placement as shown in Fig. 1, provides a uniform electric field and maximal stirring efficiency. A platinum cathode serves equally well, and becomes plated with gold during use. The generator anode is a cadmium rod, in the central tube with a medium porosity sintered glass bottom, and the anolyte is *ca.* 0.8*M* cadmium chloride in 2*M* potassium chloride.

The supporting electrolyte was cupric sulfate (usually 0.04*M*) in hydrochloric acid (1–2*M*). A concentration of cupric ion of 0.04*M* is adequate up to a generating current density of *ca.* 20mA/cm^2 when the solution is well stirred.

Air was removed from both the test solution and anolyte with nitrogen. Removal of dissolved oxygen is essential when maximal accuracy is desired. If it is not removed it competes with the gold in oxidizing the chloro cuprous ion, especially near the e.p., and a significant positive error results.

The equivalence point was detected potentiometrically in the ordinary manner[1]. In manual titrations, when the generating current is interrupted for the potential readings, the gold (or gold-plated platinum) generator cathode serves also as indicator electrode. A saturated calomel reference electrode (S.C.E. in Fig. 1) was used. In automatic titrations, using apparatus already described[5], a separate gold indicator electrode is, of course, necessary.

The generating current was automatically maintained constant to ±0.01% by the controller previously described[5]. Time was measured with a Standard Electric Time Co. model S-10 stopclock, whose precision was ±0.01 sec and whose accuracy was governed by the constancy of the frequency of the commercial 110 V a.c. supply (*ca.* ±0.05% for few minute intervals).

Standard solutions of +3 gold ($AuCl_4^-$) were prepared by dissolving pure gold in aqua regia, and evaporating twice with hydrochloric acid to a small volume on the steam bath to remove nitrogen compounds. These evaporations must not proceed to dryness, because this causes some of the gold to precipitate as the metal. Presumably this occurs via $HAuCl_4 \rightarrow AuCl + Cl_2 + HCl$, followed by partial reduction of the aurous chloride by chloride ion. With about 2 g of gold the solution may safely be evaporated to about 10 ml, when about 50 ml of concentrated hydrochloric acid is added for each evaporation. After adding additional hydrochloric acid to yield a final concentration of 0.2 to 0.5*M* the solutions were diluted to a known volume. The pipets used to dispense samples of the standard solutions were calibrated. The overall uncertainty in the volumetric measurements was about ±0.2%.

TITRATION CHARACTERISTICS

As expected from the fact that chloride ion is a product of the titration reaction (eqn. 1), the magnitude of the potential change at the equivalence point decreases with increasing chloride ion concentration. This is demonstrated by the automatically recorded titration curves in Fig. 2. That the inflection points in these curves occur somewhat later than the theoretical equivalence point is due partly to lag in the mixing of the solution but chiefly to the time required for the titration reaction to reach equilibrium. In manual titrations, in which sufficient time (*ca.* 2 min) is allowed for the reaction to reach equilibrium at each measurement point, the point of maximal rate of change of potential does agree closely with the theoretical e.p.

A marked peculiarity of the titration curve is the steady *increase* in potential up to approximately two-thirds of the theoretical e.p. time. During the latter one-third of a titration the potential decreases normally. This same increase in potential during the first two-thirds of the titration is also observed when measurements are made manually, allowing several minutes for at least approximate potential stabilization at each point. This clearly indicates that the $AuCl_4^-$ ion is reduced stepwise, first to $AuCl_2^-$ and then to the metal. This conclusion is substantiated by the fact that visible precipitation of metallic gold occurs only after the titration is more than two-thirds completed; up to this point the solution remains perfectly clear.

An increase in potential during a reductometric titration is, of course, thermodynamically anomalous, and must result from a slow approach of the gold indicator electrode to its equilibrium potential in an $AuCl_4^-$ solution. In one trial with $5.74 \cdot 10^{-3}M$ auric chloride in 1N hydrochloric acid the initial potential was +0.644 V *vs.* S.C.E. After an hour it had increased to only +0.664 V and was still rising very slowly. When the titration was then begun, the potential increased quickly and became approximately constant within about a minute at each point, and two-thirds of the way to the e.p. it attained a maximal value of +0.693 V, after which it finally decreased. Evidently, in a mixture of $AuCl_4^-$ and $AuCl_2^-$ the $AuCl_2^-/Au$ couple is potential determining and reaches its equilibrium potential quickly.

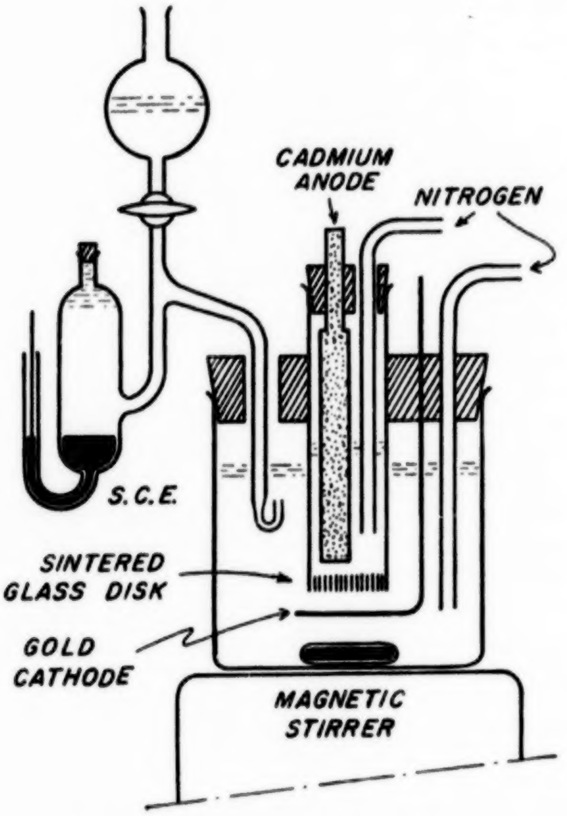

Fig. 1. Titration cell.

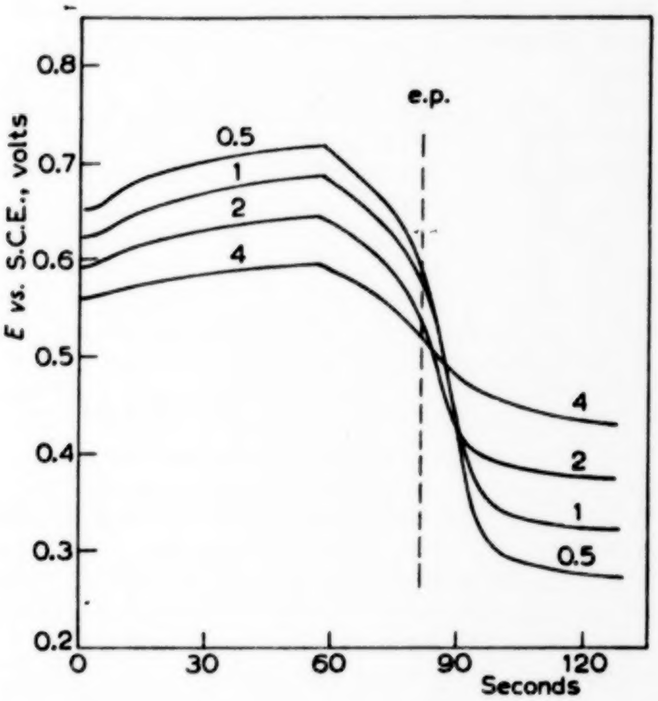

Fig. 2. Automatically recorded titration curves of 5.27 mg of +3 gold in 100 ml of 0.04M cupric sulfate with the hydrochloric acid concentration indicated by the numbers on each curve. The generating current was 94.9 mA. A separate gold wire indicator electrode (not shown in Fig. 1) was used, and the potential between it and a saturated calomel reference electrode was recorded with a recording potentiometer as a function of generation time.

From the measurements of Bjerrum and Kirschner[6]

$$AuCl_4^- + 3e \rightarrow Au + 4Cl^-;\ E^\circ = +0.758 \text{ V } vs. \text{ S.C.E.}$$

For the couple involving solid aurous chloride Latimer[7] has estimated

$$AuCl + e \rightarrow Au + Cl^-;\ E^\circ = +0.93 \text{ V } vs. \text{ S.C.E.}$$

From these values one might expect that +3 gold would be reduced directly to the metal, rather than stepwise through the +1 state. However, AuCl dissolves in the presence of chloride ion to form $AuCl_2^-$, and this doubtless is the species of +1 gold extant in the present solutions. No previous measurement of the $AuCl_2^-/Au$ potential seems to have been reported. Assuming that $AuCl_2^-$ is the predominant, potential-determining species during the last one-third of a titration, it follows from the observed potentials that

$$AuCl_2^- + e \rightarrow Au + 2Cl^-;\ E^\circ = +0.86 \text{ V } vs. \text{ S.C.E.}$$

This value is 0.07 V less oxidizing than the potential of the AuCl/Au couple, and it follows that

$$\mathrm{AuCl} + \mathrm{Cl^-} \rightarrow \mathrm{AuCl_2^-};\ K = ca.\ 15$$

which is entirely reasonable. From the value for the potential of the $AuCl_2^-$/Au couple and that for the $AuCl_4^-$/Au couple quoted above, we obtain

$$\mathrm{AuCl_4^-} + 2\mathrm{Au} + 2\mathrm{Cl^-} \rightarrow 3\mathrm{AuCl_2^-};\ E^\circ = -0.10\ \mathrm{V}$$

$$K = \frac{(\mathrm{AuCl_2^-})^3}{(\mathrm{AuCl_4^-})\ (\mathrm{Cl^-})^2} = 10^{-5}$$

From this it is evident that $AuCl_2^-$ tends to be unstable in respect to disproportionation into $AuCl_4^-$ and Au. However, the equilibrium constant is only moderately small, and its form is such that $AuCl_2^-$ is stabilized the larger is the concentration of chloride ion and especially the smaller is the *sum* of the concentrations of $AuCl_4^-$ and $AuCl_2^-$. For example, with $2M$ chloride ion, the foregoing equilibrium is displaced to the right when the total concentration of dissolved gold is smaller than $0.008M$.

In the titrations reported herein the largest initial concentration of $AuCl_4^-$ was only $0.006M$, and usually was much smaller. Therefore, it is understandable that the reduction should proceed stepwise to $AuCl_2^-$ and then to the metal.

Titrations were not attempted with less than $0.5N$ hydrochloric acid, because with much smaller concentrations of chloride ion cupric ion tends to be reduced directly to the metal rather than to $CuCl_2^-$. Although metallic copper is capable of reducing $AuCl_4^-$ the reaction is likely to be inconveniently slow.

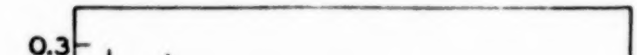

Fig. 3. Chronopotentiograms of $0.02M$ cupric sulfate in $1N$ hydrochloric acid. The cell of Fig. 1 was used, and the potential of the gold generator cathode (14 cm² area) against the S.C.E. was recorded with a recording potentiometer. The solution was unstirred. For curve 1 the generating current was 12.5 mA and for curve 2 it was 31 mA.

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From free energy data quoted by LATIMER[7]

$$Cu^{+2} + 2Cl^- + e \rightarrow CuCl_2^-;\ E^\circ = +0.222 \text{ V } vs. \text{ S.C.E.}$$

$$CuCl_2^- + e \rightarrow Cu + 2Cl^-;\ E^\circ = -0.064 \text{ V } vs. \text{ S.C.E.}$$

Both stages of the reduction proceed quite reversibly at a gold cathode, *i.e.* very little overpotential is required. This is demonstrated by the chronopotentiograms in Fig. 3. These were obtained with the regular titration cell (Fig. 1) by polarizing the gold cathode with constant current and recording its potential versus a saturated calomel reference electrode as a function of time with a recording potentiometer. The solution was unstirred. Two different polarizing currents were used in order to delineate both stages of reduction.

In agreement with the SAND relation[8] for a diffusion controlled electrode reaction the transition time for the $Cu^{+2} \rightarrow CuCl_2^-$ stage is inversely proportional to the square of the current. For a reaction of this type the potential at one fourth the transition time should be very nearly equal to the standard potential (*i.e.*, +0.222 V), and this is seen to be true.

For the 0.02*M* concentration of copper used, the second stage begins at a potential only slightly more reducing than that (—0.16 V) predicted from the standard potential of the $CuCl_2^-/Cu$ couple. The observed ratio of the second to first transition times is close to 4:1, compared to the theoretical value 3:1. This indicates that some reduction of hydrogen ion accompanies the reduction of $CuCl_2^-$.

It is evident that 100% current efficiency for $Cu^{+2} \rightarrow CuCl_2^-$ is easily obtained, provided the concentration of cupric ion is large enough with respect to the current density and conditions of stirring so that the potential of the gold cathode during generation remains at a value larger than about +0.1 V *vs.* S.C.E. Under the conditions used in this study (0.02 to 0.04*M* cupric ion and a current density of 7 mA/cm²) the working potential of the cathode was close to +0.20 V when the hydrochloric acid concentration was 1*N*, and it was a few centivolts more positive with 2*N* hydrochloric acid.

The reductions of $AuCl_4^-$ and $AuCl_2^-$ proceed both by direct electrode reaction and via electrogenerated $CuCl_2^-$, but, since the current efficiencies for both processes are 100%, the titration efficiency is 100% regardless of their relative proportions.

ANALYTICAL DATA

Typical data obtained in titrating 1 to 113 mg of +3 gold in *ca.* 100 ml of air-free supporting electrolyte are shown in Table I. The supporting electrolyte was pre-titrated to the e.p. before the gold sample was added.

These data were obtained with several standard auric chloride solutions, whose concentrations were such that the desired quantity of gold could be dispensed with either a 5-, 10-, or 25-ml pipet. Thus the percentage error in measuring out the smallest samples was no greater than with the larger, and in all cases was *ca.* ±0.2%. The average titration error of ±0.3% does not differ significantly from the probable error of sample measurement.

TABLE I

TITRATION DATA

The supporting electrolyte (volume 100 ml) was 0.04*M* in respect to cupric sulfate and either 1 or 2*N* in hydrochloric acid. The generating current was 94.90 ± 0.01 mA, and the area of the gold generator cathode was 14 cm^2, 1 sec at 94.90 mA = 0.06458 mg Au.

Gold taken mg	*Titration time sec*	*Gold found mg*	*Error mg*	*Error %*
113.04	1752.1	113.17	0.13	0.1
45.08	702.0	45.34	0.26	0.6
	698.1	45.09	0.01	0.0
	698.4	45.11	0.03	0.1
	699.6[a]	45.18	0.10	0.2
26.35	406.8	26.27	—0.08	—0.3
	407.5	26.32	—0.03	—0.1
22.62	352.5	22.77	0.15	0.7
5.272	81.9	5.289	0.017	0.3
	81.4	5.257	—0.015	—0.3
1.051	16.23[a]	1.048	—0.003	—0.3
	16.26[a]	1.050	—0.001	—0.1
				Av. ±0.3

In 1*N* HCl. All others in 2*N* HCl.

The accuracy of the titration was verified further by alternate anodic and cathodic generation. When the gold electrode is subjected to anodic polarization the gold enters solution as $AuCl_2^-$, and this can then be titrated by reversing the polarity of the electrode and generating cathodically to the e.p. at +0.520 V *vs.* S.C.E. The results of four such trials with a generating current of 94.86 mA in 0.04*M* cupric sulfate-1*N* hydrochloric acid were:

Anodic generation, sec	20.0	100.0	300.0	600.0
Cathodic titration, sec	20.0	100.5	300.5	600.8
Error, sec	0.0	+0.5	+0.5	+0.8

In similar trials with 2*N* instead of 1*N* hydrochloric acid the results were:

Anodic generation, sec	20.0	100.0	300.0	600.0
Cathodic titration, sec	19.8	99.1	299.8	599.8
Error, sec	—0.2	—0.9	—0.2	—0.2

In both 1 and 2*N* hydrochloric acid, with 0.04*M* cupric sulfate, the equivalence point potential is +0.520 V *vs.* S.C.E., independent of the quantity of gold, and from many titrations its reproducibility is conservatively estimated as ± 0.005 V. With 2*N* hydrochloric acid the rate of potential change at the e.p. is *ca.* 45 mV/sec at 95 mA with 100 ml of solution. Hence an uncertainty of ±0.005 V corresponds to ±0.1 sec or ±0.006 mg of gold. With 1*N* hydrochloric acid the rate of potential change at the e.p. is *ca.* 140 mV/sec at 95 mA with 100 ml of solution, and an uncertainty of ± 0.005 mV is equivalent to ±0.04 sec or ±0.002 mg of gold. It should not be difficult to titrate as little as 0.1 mg of gold with an error within ±1% if the volume of supporting electrolyte were decreased to about 20 ml.

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Fortunately the titration can be applied in the presence of the two elements, copper and silver, most commonly associated with gold. Most of the silver will be precipitated as silver chloride in preparing the sample solution, and the small concentration of $AgCl_2^-$ remaining in solution is not reduced by chloro cuprous ion. Indeed, it is not even necessary to remove the precipitated silver chloride, provided it is protected from light decomposition. In one experiment in which 350 mg of silver nitrate was added the error in the titration of 6 mg of gold was —0.6%. This experiment also demonstrates that nitrate ion at a concentration of 0.02*M* does not interfere.

Mercury (added as $HgCl_2$) in amounts up to 200 mg did not interfere, and considerably larger amounts probably would also be innocuous.

Since lead does not interfere, the titration is applicable to the lead-gold alloy obtained by fire assay methods, provided platinum group metals are not present.

Of the platinum metals, ruthenium, palladium, rhodium, iridium, and osmium probably will all interfere when present in their highest oxidation states because their potentials are all at least as or more oxidizing than the potential of the $AuCl_2^-/Au$ couple. The standard potentials of the pertinent platinum couples are[7]

$$PtCl_4^{-2} + 2e \rightarrow Pt + 4Cl^-;\ E^\circ = +0.51 \text{ V } vs. \text{ S.C.E.}$$

$$PtCl_6^{-2} + 2e \rightarrow PtCl_4^{-2} + 2Cl^-;\ E^\circ = +0.44 \text{ V } vs. \text{ S.C.E.}$$

Since these values are well below (less oxidizing than) the $AuCl_2^-/Au$ potential it was expected that an e.p. for the titration of gold could be obtained before reduction of either $PtCl_6^{-2}$ or $PtCl_4^{-2}$ began. Because the potential of the $PtCl_4^{-2}/Pt$ couple is more oxidizing than that of the $PtCl_6^{-2}/PtCl_4^{-2}$ couple, one would expect that $PtCl_6^{-2}$ would be reduced directly to the metal by chloro cuprous ion rather than to $PtCl_4^{-2}$. Only the first of these expectations was realized.

Curve 1 in Fig. 4 shows the titration curve of 5.272 mg of +3 gold in the presence of 27.2 mg of $(NH_4)_2PtCl_6$ in 100 ml of 0.04*M* cupric sulfate-1*N* hydrochloric acid.

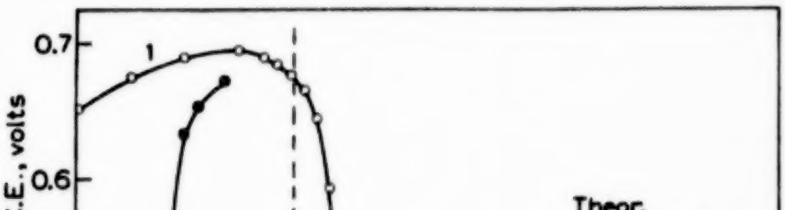

Fig. 4. Titration of a mixture of 5.27 mg of +3 gold and 12.0 mg of +4 platinum with a generating current of 94.9 mA in 100 ml of 0.04*M* cupric sulfate - 1*N* hydrochloric acid. Curve 2 was obtained by back titrating the solution from curve 1 after the polarity of the gold generator electrode was reversed.

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Although the e.p. for gold is well defined, it is subject to a large positive error which increases with the quantity of platinum present. Presumably $PtCl_6^{-2}$ competes with $AuCl_2^-$ in the oxidation of chlorocuprous ion, and the $PtCl_4^{-2}$ produced reduces $AuCl_2^-$ only very slowly if at all. Satisfactory titrations of gold in the presence of +4 platinum can be expected only when the amount of platinum is less than half the quantity of gold. Presumably, +2 platinum would not interfere, but this has little practical significance because the methods usually used to prepare solutions of gold samples will leave the platinum in the +4 state.

Contrary to prediction based on the standard potentials, reduction of $PtCl_6^{-2}$ proceeds only to $PtCl_4^{-2}$ rather than to the metal. This confirms the observation of GRINBERG AND GOL'BRAĬKH[9] that $PtCl_4^{-2}$ is not readily reduced by excess cuprous chloride.

The second e.p. coincides fairly well with the *sum* of gold and platinum, but the direct titration is very inconvenient because a long time is required for the attainment of steady potential readings during the titration of the $PtCl_6^{-2}$. A more practical procedure is to generate excess chloro cuprous ion, and then reverse the polarity of the gold generator electrode and back titrate with electrogenerated $AuCl_2^-$. Curve 2 in Fig. 4 was obtained by back titrating in this way the solution from curve 1. Note that curve 2 shows no break for oxidation of $PtCl_4^{-2}$ to $PtCl_6^{-2}$, which confirms the postulate that $PtCl_4^{-2}$ reacts only very slowly with $AuCl_2^-$. The theoretical e.p. for this back titration is 250—206 = 44 sec, whereas the observed e.p. is at 35 sec. Apparently a small fraction of the $PtCl_4^{-2}$ is reduced to metallic platinum by excess chloro cuprous ion.

SUMMARY

A method for the coulometric titration of +3 gold to the metallic state with electrolytically generated chloro cuprous ion is described. Quantities of gold from as little as 1 mg to 100 mg or more were titrated in a volume of 100 ml with an average error of ±0.3%.

The titration is applicable to the determination of gold in the presence of large amounts of copper, silver, mercury, lead, and most of the elements with which gold commonly is associated. Small amounts of +4 platinum (less than half the amount of gold) are innocuous, but larger quantities of platinum produce a large positive error.

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Received February 17th, 1958

POTENTIOMETRIC DETERMINATION OF POTASSIUM FERRICYANIDE

by

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There are hardly any references in the literature to the potentiometric investigation of the simple reaction between $AgNO_3$ and $K_3[Fe(CN)_6]$ and hence the present investigation was initiated. KHOSLA AND GAUR[1] mention the possibility of determining $K_3[Fe(CN)_6]$ by polarography.

EXPERIMENTAL

Merck's guaranteed extra pure reagents, $AgNO_3$ and $K_3[Fe(CN)_6]$, were used and the strengths of the solutions were further checked by standard methods of analysis. Different concentrations of the two salts in solution were used and potentiometric titrations were carried out both by the direct and the reverse methods, *i.e.*, the $K_3[Fe(CN)_6]$ solution was added from the micro-burette to the $AgNO_3$ solution in the electrode cell and *vice versa*. For precise and steady measurements of e.m.f., a platinum gauze electrode was used. This was electrolytically coated with silver at a low current density (current strength of the order of 2–10 mA) in a bath of pure potassium silver cyanide. It was dipped in the titre solution and used as an indicator electrode in conjunction with a saturated calomel electrode. The connexion between the calomel half-cell and the titration vessel was made with saturated KNO_3 solution. The electrode cell was immersed in an electrolytically maintained thermostat. The e.m.f. was measured on a Cambridge (null-deflection type) pH meter. The titre solution was continuously stirred by an electrically driven stirrer. Curves were plotted of the E (obs.) *vs.* the volume of the titrant added in ml, and from the sharp jump in potential indicated by the titration curves, the equivalence point was obtained. This was further checked by calculating the maximum value of dE/dV in each case. The titrations were also carried out in the presence of varying concentrations of ethanol and NH_4NO_3; 20 ml of the reagent was taken in the cell each time (see Table I).

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TABLE I

SUMMARY OF RESULTS OF POTENTIOMETRIC TITRATIONS

Molarity of $K_3[Fe(CN)_6]$ solution	*Molarity of $AgNO_3$ solution*	*Points of equivalence ml of $K_3[Fe(CN)_6]$ or $AgNO_3$ solution required for the formation of $Ag_3[Fe(CN)_6]$*			
		Calculated	*Obtained from max. dE/dV in presence of*		
			ethanol 0%	*ethanol* 20%	*NH_4NO_3* 1 g
		Direct titrations (Figs. 1–4)			
M/4	*M/12*	2.22	2.21	2.22	2.22
M/10	*M/20*	3.33	3.32	3.34	3.33
M/40	*M/100*	2.66	2.64	2.68	2.70
M/150	*M/250*	4.0	3.98	4.0	3.96
		Reverse titrations (Figs. 5–8)			
M/50	*M/2.5*	3.0	3.02	3.0	3.02
M/150	*M/10*	4.0	4.0	4.0	4.0
M/400	*M/25*	3.75	3.78	3.80	3.80
M/1000	*M/100*	6.0	6.10	6.05	6.0

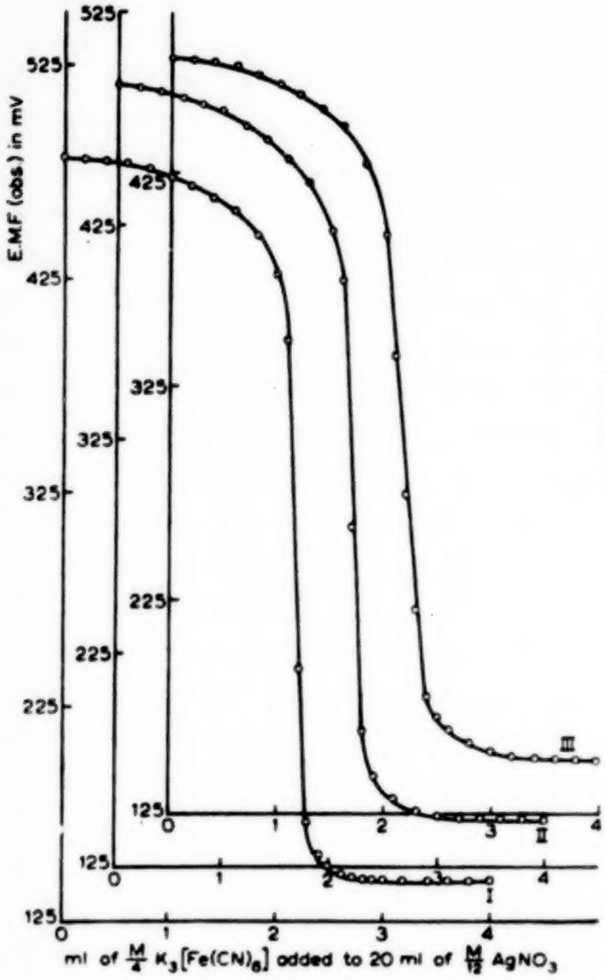

Fig. 1. Direct titrations. Curve I refers to 0% alcohol, curve II to 20% alcohol, curve III to 1 g NH_4NO_3.

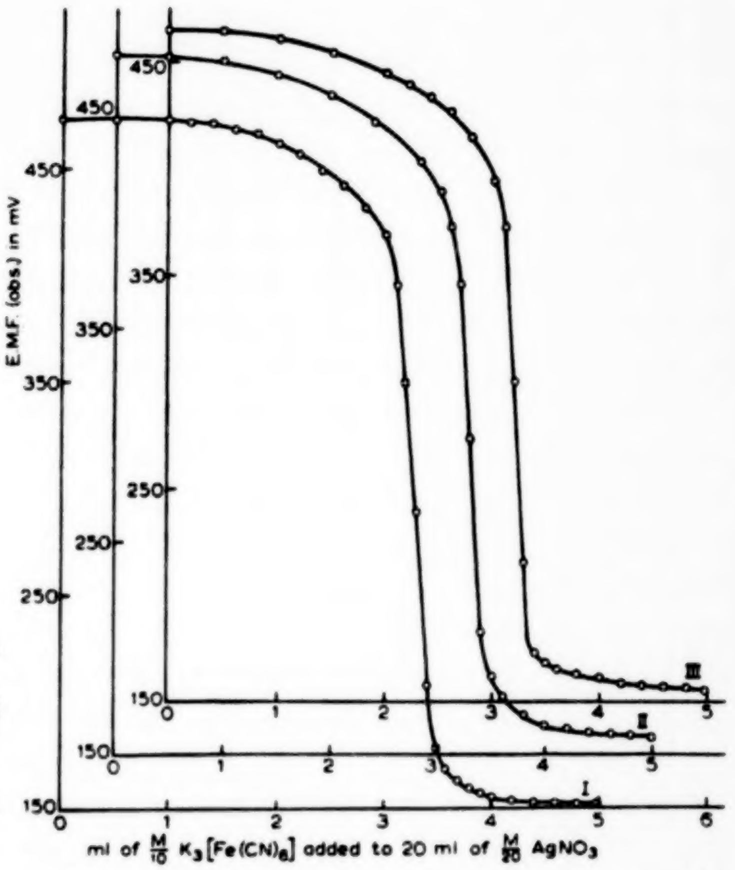

Fig. 2. Direct titrations. Curve I refers to 0% alcohol, curve II to 20% alcohol, curve III to 1 g NH_4NO_3.

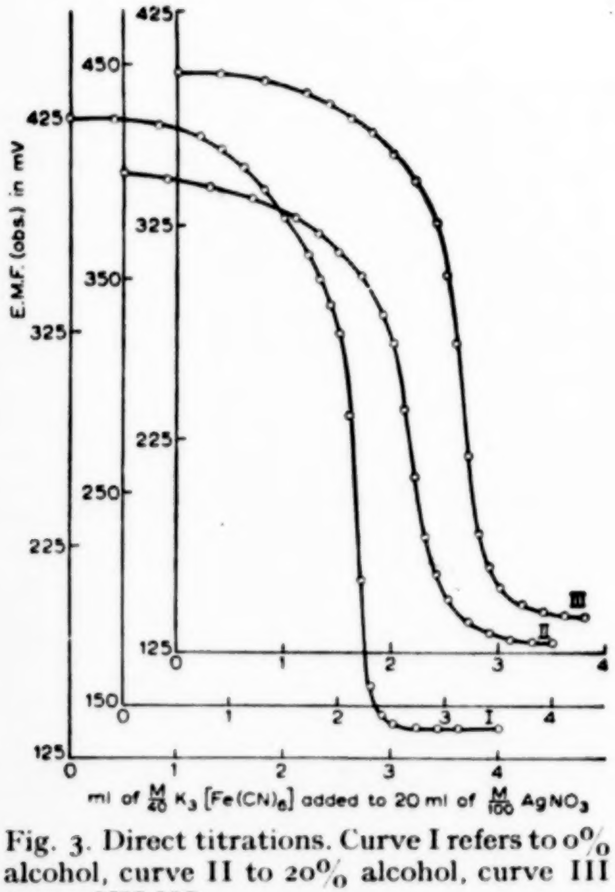

Fig. 3. Direct titrations. Curve I refers to 0% alcohol, curve II to 20% alcohol, curve III to 1 g NH_4NO_3.

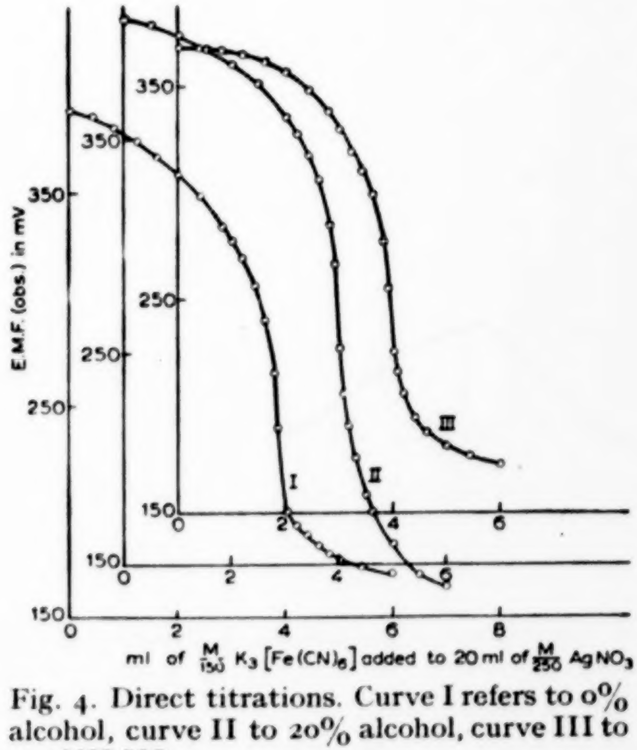

Fig. 4. Direct titrations. Curve I refers to 0% alcohol, curve II to 20% alcohol, curve III to 1 g NH_4NO_3.

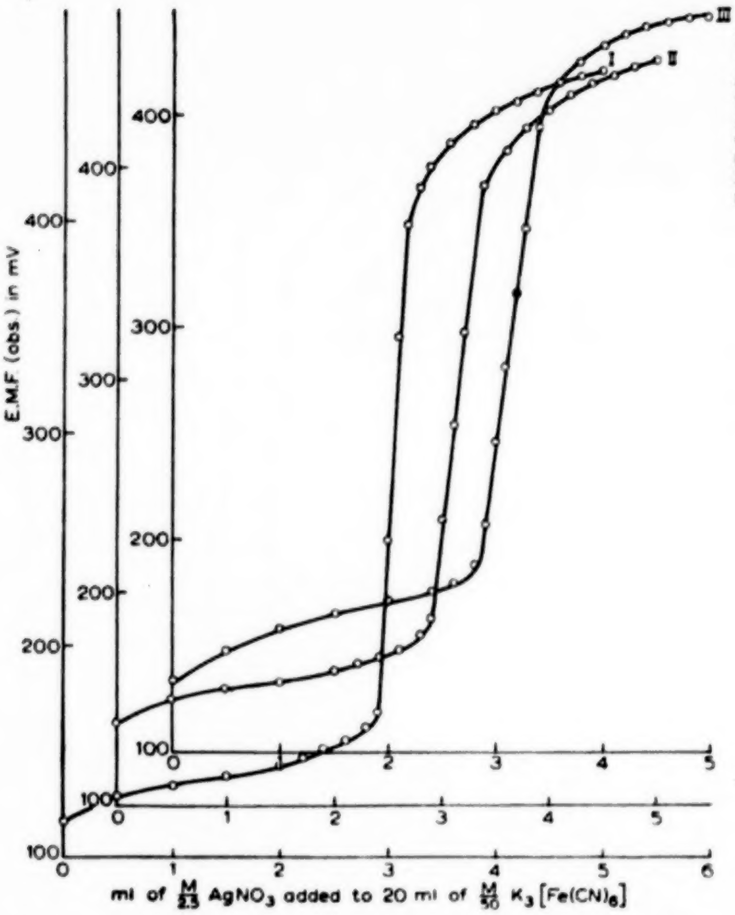

Fig. 5. Reverse titrations. Curve I refers to 0% alcohol, curve II to 20% alcohol, curve III to 1 g NH_4NO_3.

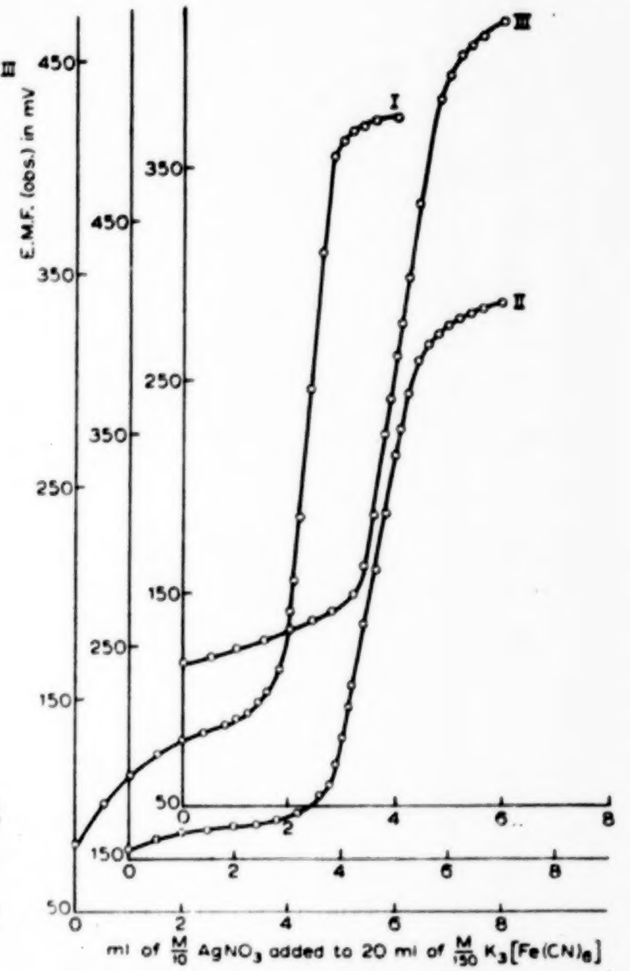

Fig. 6. Reverse titrations. Curve I refers to 0% alcohol, curve II to 20% alcohol, curve III to 1 g NH_4NO_3.

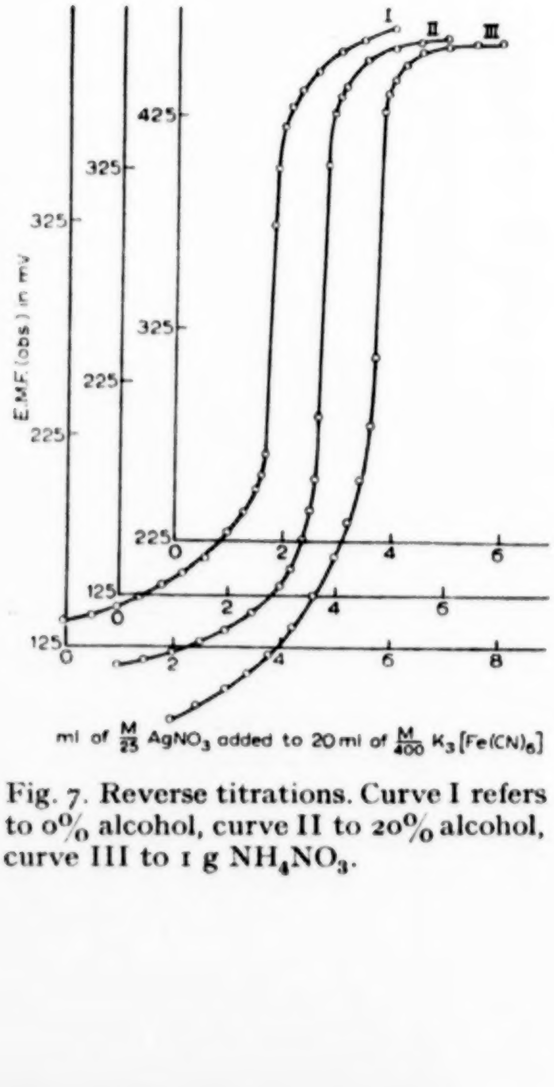

Fig. 7. Reverse titrations. Curve I refers to 0% alcohol, curve II to 20% alcohol, curve III to 1 g NH_4NO_3.

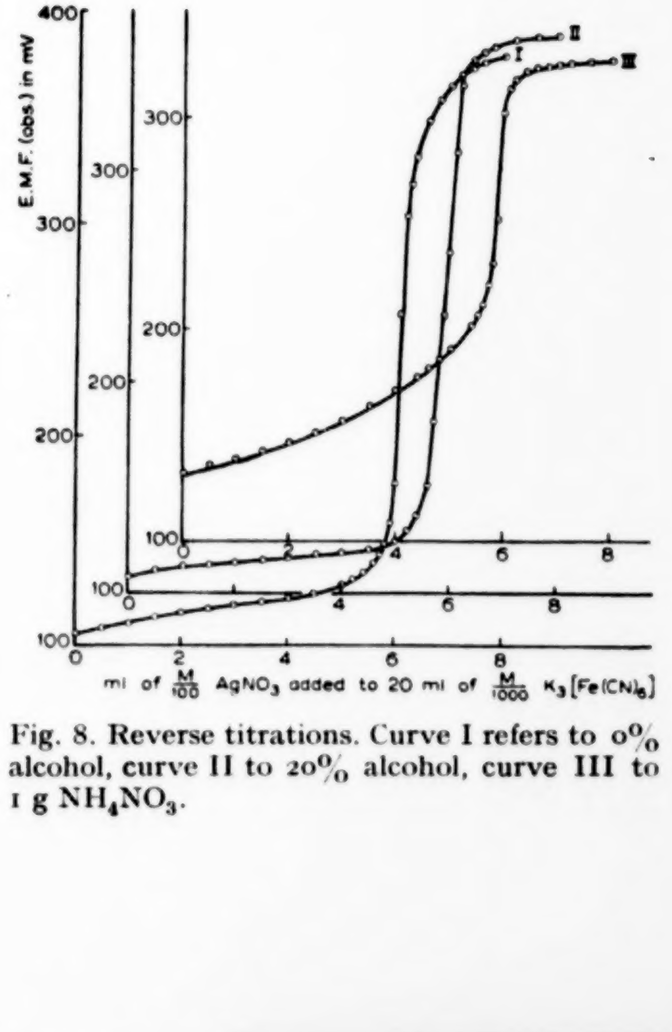

Fig. 8. Reverse titrations. Curve I refers to 0% alcohol, curve II to 20% alcohol, curve III to 1 g NH_4NO_3.

DISCUSSION

It is clear from Figs. 1–8 and Table I that the reaction between $AgNO_3$ and $K_3[Fe(CN)_6]$ can be successfully followed potentiometrically using silver as an indicator electrode with either of the reactants alternately used as the titre. The end-point obtained from the maximum dE/dV and from the deflection in the curves, occurs at a point where the molecular ratio of the reagents ($K_3[Fe(CN)_6]$ and $AgNO_3$) is 1:3, corresponding to the formation of the compound $Ag_3[Fe(CN)_6]$. The titration curves are symmetrical on both sides of the equivalence point, which is marked by a sharp change in e.m.f., and the results are very accurate and reproducible.

On adding $AgNO_3$ to $K_3[Fe(CN)_6]$, an orange-coloured precipitate is first formed which settles down quickly after the end-point has been reached and this change is so sharp that the equivalence point can be accurately detected visually.

In the direct titrations, when the silver electrode is dipped into $AgNO_3$ solution, the e.m.f. assumes a steady value rapidly after each addition of $K_3[Fe(CN)_6]$ solution, till at the end-point a sharp fall in potential is observed, after which the e.m.f. becomes constant again. The whole titration takes little time. In the reverse titrations, however, the e.m.f. rises from the beginning of the reaction and a marked upward jump occurs at the point of equivalence. In the neighbourhood of the end-point it takes a little time for the potential to reach a constant value. Continuous stirring in the vicinity of the electrode has a favourable effect on the titration.

The addition of ethanol or electrolytes such as NH_4NO_3 has hardly any effect on the accuracy of the end-point or on the magnitude of the break in potential.

The potentiometric method is simple, rapid and accurate and offers a means of determining even low concentrations of ferricyanide or silver as accurately as other methods.

SUMMARY

A rapid and accurate electrometric method for the determination of potassium ferricyanide solutions has been investigated. It consists in titrating ferricyanide solutions potentiometrically against standard $AgNO_3$, using a silver indicator electrode in conjunction with a saturated calomel electrode connected by a KNO_3 bridge. Either of the reagents may be used as the titrant. A marked change in e.m.f. is observed at the end-point corresponding to the formation and precipitation of $Ag_3[Fe(CN)_6]$. The curves have a regular form, a pronounced maximum in dE/dV occurs at the end-point and the results are very accurate and reproducible. The reaction, though simple, affords a quantitative method for the determination of ferricyanide or silver. The effect of neutral salts and ethanol on the accuracy of the end-point has been studied.

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Received February 13th, 1958

THE POLAROGRAPHIC DETERMINATION OF ALUMINIUM*

VI. THE ELIMINATION OF INTERFERING ELEMENTS AND THE DETERMINATION OF ALUMINIUM BY OSCILLOGRAPHIC POLAROGRAPHY

by

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INTRODUCTION

In this series of papers the polarography of aluminium has been reviewed[1] and extensive studies of the azo-dye method of WILLARD AND DEAN[2] have been described[3]. The use of this method for the determination of traces of aluminium in beryllium has also been reported[4].

In view of the high sensitivity and low upper limit of determination of the azo-dye method a further investigation was undertaken to establish conditions for the determination of aluminium by oscillographic polarography, using a calcium chloride base electrolyte. Since the procedure developed[5] involved the measurement of the height of an aluminium peak occurring at a potential in the region of —1.7 V it was evident that the wave would be preceded by, and suffer interference from, many commonly-occurring ion species. The work described in this report was undertaken to study these interferences and to provide a procedure for their elimination, which could be used under the conditions already established for the determination.

EXPERIMENTAL

All polarography was carried out at 25° on the linear-sweep cathode ray polarograph[6,7] and *versus* the mercury pool anode. All potentials are quoted on the European sign convention. On this convention the potential of the saturated calomel electrode (S.C.E.) has been taken as + 0.246 V *versus* the normal hydrogen electrode (N.H.E.).

Ion interferences

Experiments were made with a large series of solutions to study the effect of other ion species on the polarography of aluminium under the conditions previously established[5]. Each solution was prepared as follows: A 5-ml portion of 0.2M calcium chloride solution was treated with an aliquot of solution containing 100 μg of aluminium and with a known amount of one of the ion species under investigation. After neutralisation, if necessary, with sodium hydroxide 0.1 ml of 0.05M potassium hydrogen phthalate was added and the solution diluted to about 9.5 ml. The pH value was then adjusted to 4.0 by addition of hydrochloric acid and the solution made up to 10 ml in a graduated flask.

An aliquot of each solution was deoxygenated, by bubbling hydrogen through it for 10 min, and polarographed. The effects on the aluminium wave of each ion species examined are described below.

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Nickel. A slight enhancement of the aluminium peak height was detected when the ratio of nickel to aluminium was 2:1. This did not exceed a 10% increase in peak height when the ratio was 5:1, but became serious when the excess was tenfold. It was noted that the interference caused alteration in shape at the foot of the aluminium wave, indicating, as would be expected, that the enhancement was caused by a previous reduction of the nickel ion. The change in shape of the aluminium step is shown in Fig. 1.

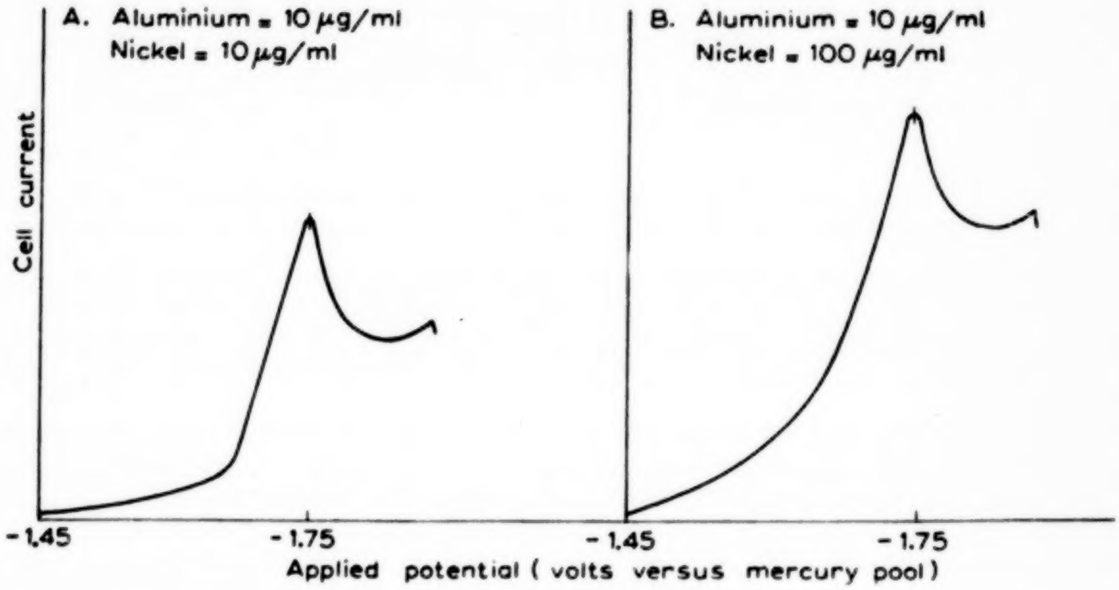

Fig. 1. Effect of nickel on the wave due to aluminium in 0.1 M calcium chloride.

Ferric iron. This species did not cause interference until present in an amount 10 times that of the aluminium. At iron concentrations above this value the aluminium peak height was progressively depressed until, at 100-fold excess, no aluminium step was obtained.

During the preparation of these solutions much of the iron was precipitated by the addition of sodium hydroxide to bring the pH of the final solution to 4. Some iron, however, remained in solution, since a brown colour remained even after centrifuging. It seems probable that the decrease in aluminium peak height was due to co-precipitation of this element with the iron.

Ferrous iron. No interference was caused until ferrous iron was present in a concentration 5 times that of the aluminium. A steady enhancement of the aluminium peak height then occurred, which amounted to almost 50% when the iron concentration was 25 times that of aluminium.

Zinc. The presence of zinc caused serious interference at all concentrations. This amounted to an enhancement in peak height of more than 20% when the zinc–aluminium ratio was only 2:1.

Chromium. In the trivalent state chromium gave a peak at a potential more positive than that due to aluminium. It was, however, sufficiently close to cause interference with the foot of the aluminium wave. At low chromium concentrations this had the effect of enhancing the aluminium peak height, but at higher concentrations (5 times that of aluminium) the chromium wave became well-defined and then caused an apparent decrease in the aluminium peak height. At chromium–aluminium ratio 10:1 this amounted to 25%.

Manganese. This element did not interfere with the aluminium peak until its concentration ratio was 10:1. At this ratio the aluminium peak height was depressed by about 10%.

Fluoride. Fluoride ion had, in general, a depressive effect on the aluminium peak. When the fluoride–aluminium ratio was 10:1 the aluminium wave was completely suppressed. At low fluoride concentrations, however, the aluminium peak appeared to be enhanced. This was seen to be due to the fact that the addition of fluoride caused the peak potential to shift from —1.72 V *versus* the mercury pool to —1.83 V. Interference was thus encountered from a wave at about —1.9 V, probably due to the reduction of the base electrolyte.

Removal of interfering ions

Mercury cathode electrolysis. Experiments were carried out to ascertain whether some, or all of the above-mentioned metal ions could be removed by electrolysis at a stirred mercury cathode. The apparatus employed was that described earlier in this series[4]. The solutions employed contained 20 μg/ml of aluminium in the presence of 200 μg/ml of the interfering element. They were treated as already described.

It was found that electrolysis for 30 min, at the stirred mercury cathode at a potential of —1.5 V *versus* a silver–silver chloride anode, was sufficient to remove zinc, iron and nickel interference. The interference due to large concentrations of manganese was reduced to negligible proportions.

Polarography of these solutions, and of electrolysed solutions containing aluminium alone, showed that a reduction in the height of the aluminium peak also occurred under the conditions that had been employed. It was also found that the pH of the solutions was affected. In solutions containing the interfering species alone the pH usually fell, often to below 3. In solutions containing aluminium the pH rose, in some cases to values as high as 6.7. All solutions were therefore re-adjusted to pH 4 before polarography. The aluminium solutions which had suffered larger rises in pH gave much reduced aluminium recoveries and in the case of solutions of pH 6.7 no aluminium wave was obtained.

In order to overcome this difficulty the pH of the solutions was adjusted to pH 3, instead of 4, before electrolysis. Under these conditions electrolysis at —1.5 V for 30 min never caused the pH to rise above 4.3 and the aluminium recoveries were better than 95%. In addition chromium interference was now also removed, whereas previously, at pH 4, this had not been found possible.

Fluoride ions. A number of methods for separating aluminium from fluoride, or for eliminating its interference were tried. None was successful.

The most promising procedure involved the precipitation of the aluminium with ammonium hydroxide, followed by careful washing and dissolution in hydrochloric acid. The polarographic procedure already established[6] was then applied. Very poorly-shaped aluminium waves were obtained.

Further experiments revealed the surprising fact that, although poor results were obtained by polarography, separation from fluoride was virtually complete. This was confirmed by the discovery that the poorly-shaped waves could be produced if the separation procedure was applied to aluminium solutions, from which fluoride was absent. It was also noted that the aluminium wave, whose peak occurred at a potential of —1.75 to —1.80 V, *versus* the mercury pool, under these conditions was suffering interference from the foot of the base electrolyte reduction wave at —1.95 V. This largely accounted for the poor shape.

In an attempt to prove that the base electrolyte was responsible for the interference the experiments were repeated in 0.1*N* potassium chloride. This reduced the interference, but recoveries of aluminium from fluoride solutions were still poor and this work was therefore abandoned.

METHOD

Details of the resulting method for the determination of aluminium in the presence of interfering cations are as follows:

Place an aliquot of a solution of the sample in a 100-ml beaker (Note 1). Add 15.5 ml 0.4 *M* calcium chloride solution and 0.38 ml 0.05*M* potassium hydrogen phthalate (Note 2). Dilute to 20 ml with water and adjust the pH to 3.0 by addition of hydrochloric acid or sodium hydroxide. Transfer to a 25-ml graduated flask and make up to the mark with water.

Place a mercury pool in the electrolysis cell (Note 3) and adjust the height of the stirrer so that the blades are partly immersed in the mercury surface. Transfer the solution to the cell and electrolyse for 30 min at a cathode potential of —1.5 V *versus* the silver–silver chloride electrode, measured by means of a pH meter set to read millivolts. At the conclusion of the electrolysis run off the mercury pool with the potential difference still applied to the electrodes. Transfer 10 ml of solution to a 100-ml beaker, adjust the pH to 4.0, by addition of hydrochloric acid, or sodium hydroxide and make up to volume with water in a 25-ml graduated flask.

Place an aliquot of the prepared solution in a polarographic cell and deoxygenate by bubbling hydrogen or nitrogen through it for 10 min. Then, with the start potential control of the linear-sweep cathode ray polarograph set at —1.45 V, obtain an aluminium wave on the screen. Measure the height of the aluminium peak, which occurs at about —1.75 V *versus* the mercury pool anode.

Obtain the concentration of aluminium in the sample solution by reference to one of the three calibration graphs prepared as described below.

Notes

1. The volume of sample solution taken should be such that the concentrations of aluminium in the final solution falls within one of the three calibration ranges; 20–100, 10–50 or 0–10 μg aluminium per ml.

2. These additions provide the required base electrolyte constitution (approx. 0.1 M calcium chloride and $1 \cdot 10^{-3} M$ potassium hydrogen phthalate) in the final solution.

3. Full details of the electrolysis apparatus recommended for this determination are given in a previous paper[4].

Calibration

Place 5 ml 0.2 M calcium chloride solution in each of a series of 100-ml beakers and add an aliquot of standard aluminium solution to each beaker so that the following concentrations of aluminium in the final solutions are:

(a) 0, 0.5, 1.0, 2.0, 5.0 and 10.0 μg aluminium per ml.
(b) 0, 5, 10, 25 and 50 μg aluminium per ml.
(c) 0, 25, 50, 75 and 100 μg aluminium per ml.

Neutralise each solution, if necessary, by addition of 0.1 N sodium hydroxide, add 0.15 ml 0.05 M potassium hydrogen phthalate and dilute to about 9.5 ml with water. Adjust the pH of each solution to 4.0 by addition of hydrochloric acid, transfer to 10-ml graduated flasks and make up to volume with water.

Deoxygenate and polarograph an aliquot of each solution exactly as described above, in the Method, using a single setting of polarographic sensitivity for each of the three concentration ranges.

Plot a calibration graph of aluminium peak height *versus* concentration for each concentration range.

A typical aluminium wave is shown in Fig. 2.

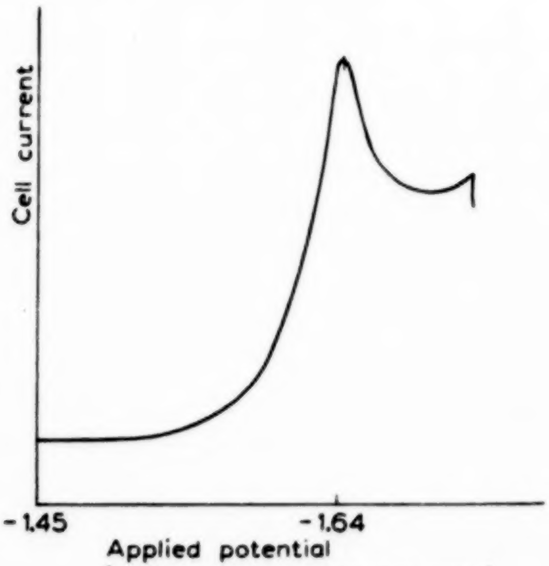

Fig. 2. Aluminium (48 μg/ml) after removal of interfering elements by mercury cathode electrolysis.

TRIAL OF THE METHOD

In order to check the accuracy and reproducibility of the method described above a series of "mock" sample solutions was prepared containing various concentrations of aluminium, iron, copper, nickel, chromium, manganese, tin and lead. Details of the constitution of the solutions and the recoveries obtained are given in Table I below.

TABLE I

Constitution of sample solution (µg/ml)								*Volume sample solution taken (ml)*	*Aluminium found (µg/ml)*
Al	*Fe*	*Cu*	*Ni*	*Cr*	*Mn*	*Sn*	*Pb*		
12000	1000	500	500	500	500	—	—	0.5	12250
6000	1000	500	500	500	500	—	—	1.0	6060
1500	1000	500	500	500	500	—	—	4·0	1560
1200	1000	—	—	—	500	500	—	5·0	1140
6000	1000	1000	500	500	—	—	250	0.5	5940
3000	2000	—	—	—	1000	—	—	1.0	3030
1500	1000	500	—	—	500	—	—	2.0	1450
600	1000	500	500	500	500	500	500	5·0	640
3000	1000	500	—	—	—	—	—	0.5	2970
750	2000	—	500	500	—	—	—	2.0	730
375	1000	500	—	—	—	250	250	4·0	380
300	1000	—	500	500	—	250	250	5·0	295
750	1000	500	500	500	250	250	250	4·0	740
600	1000	1000	—	—	—	—	—	5·0	600
1500	1000	1000	—	—	—	—	—	1.0	1480
750	1000	500	500	500	500	—	—	2.0	760
375	1000	—	—	—	—	—	—	4·0	380
1200	1000	—	—	—	—	—	—	0.5	1180
600	1000	—	—	—	—	—	—	1.0	600
300	2000	1000	500	500	500	500	250	2.0	305
120	500	—	—	—	—	—	—	5·0	125
600	1000	500	500	500	500	500	250	0.5	545
150	1000	—	500	500	—	—	—	2.0	160
75	500	500	250	250	—	—	250	4·0	78
60	500	—	—	—	500	—	—	5·0	57
1200	1000	500	500	500	—	—	—	0.5	1140
150	500	—	—	—	500	—	—	4·0	155
600	1000	500	—	—	500	500	500	0.5	560
300	1000	—	—	—	1000	—	—	1.0	310
75	500	500	500	500	250	250	500	4·0	75
60	500	—	—	—	—	—	—	5·0	58
0	500	500	500	500	500	500	500	2.0	5
150	500	500	—	—	500	—	—	1.0	160
75	250	—	—	—	250	—	—	2.0	78
37·5	200	100	100	100	—	—	—	4	40
30	200	—	—	—	100	—	—	5	32
120	200	100	—	—	100	—	—	0.5	136
30	100	—	100	100	—	—	100	2	34
15	100	—	—	—	100	—	—	4	19
12	100	50	100	100	—	—	50	5	13
30	100	—	—	—	50	50	—	1	38
15	100	—	50	50	50	—	—	2	18
7·5	100	—	—	—	—	—	—	4	9·5
6.0	100	—	25	25	—	—	25	5	8.0

DISCUSSION

The experiments carried out as described show that, as would be expected, almost all the ion species investigated interfere. Their removal by mercury cathode electrolysis is, however, satisfactory, provided that conditions are chosen so that large rises in pH value during the electrolysis are avoided.

Determination of aluminium in solutions containing fluoride ion was not achieved, although separation from fluoride appeared complete. In view of this it should be possible to establish conditions, after the separation procedure, which would allow satisfactory determination. This will be the subject of further study.

The results, presented in Table I, show that, by suitable choice of volume of sample solution taken, and of calibration range employed, it is possible after the removal of the said interfering elements to determine aluminium concentrations from 12 mg–6 μg/ml. The form of the results does not allow rigorous statistical treatment but a study of the effect of taking different volumes of sample solution shows that this has no significance at the 5% level of probability.

Statistical treatment also shows that there is a significant difference in the variabilities of the highest and lowest calibration ranges (1.12 and 1.62) compared with the middle range (0.15) at the 5% level of probability. These results therefore indicate that, if possible, the volume of sample solutions initially taken should be such that the final determination may be made on the middle range.

It is also shown that the final result is not affected by the nature and concentration of other metal ion species initially present. The range of materials to which this method is applicable is therefore very wide.

SUMMARY

A study is reported of the effect of some ion species on the determination of aluminium by oscillographic polarography under the conditions previously established. The development of an electrolytic procedure for the removal of interfering metal ions is described and details of unsuccessful attempts to remove interference by fluoride are given. The method for the determination of aluminium is given in detail and results obtained with it are presented.

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Received January 17th, 1958

REVUES DE LIVRE

Ausgewählte moderne Trennverfahren zur Reinigung organischer Stoffe par H. **Röck**, Steinkopf, Darmstadt, 1957, 33 tables, 114 figs., viii + 169 pp., cartonné: DM 24.—.

Le deuxième volume de la collection „*Progrès de la Chimie Physique*" (*Fortschritte der Physikalischen Chemie*, 1ère monographie: *Diffusion*), éditée par les soins du Prof. W. **Jost**, de Göttingen, étudie diverses techniques de séparation, destinées à la préparation de composés organiques purs. Ces méthodes sont: la fusion par zones (zone melting, 12 pp.), la chromatographie d'adsorption avec déplacement par phase liquide (21 pp.), la chromatographie de développement par phase gazeuse mobile (63 pp.) et la thermodiffusion en milieu liquide (25 pp.).

L'auteur décrit les appareillages demandés par ces procédés délicates, de jour en jour plus utilisés, et établit les corrélations utiles entre le fonctionnement de ces appareillages et les relations théoriques nécessaires à l'interprétation correcte des mesures. Une introduction, formant le premier chapitre de la monographie (35 pp.), traite d'une manière générale des problèmes de séparation par équilibres physico-chimiques. L'auteur prend pour bases communes aux diverses méthodes la loi de Raoult généralisée, le concept d'activité, la définition précise d'un facteur de séparation et la notion d'étage de séparation; grâce à l'analogie avec la théorie de la colonne de distillation et à la notion de hauteur équivalente à un étage de séparation, on parvient, par les méthodes classiques de la thermodynamique chimique, aux équations utiles, établies avec des notations claires et usuelles, reliant les fractions molaires (ou les concentrations molaires) des impuretés des mélanges de départ à celles du corps purifié.

Cette introduction traite également de l'analyse thermique comme critère de vérification du degré de pureté d'une substance organique, même en l'absence du corps rigoureusement purifié. La chromatographie avec phase gazeuse est l'occasion d'une discussion approfondie des conditions réelles de fonctionnement des colonnes et du degré de séparation maximum théorique, justifiée par l'importance considérable que prend cette technique, qui permet d'obtenir commodément des colonnes d'un nombre très élevé d'étages de séparation.

Il faut encore mentionner que cet ouvrage a été rédigé pour l'usage industriel comme pour celui du laboratoire spécialisé et que le chimiste analyste y trouvera de très précieuses indications. Les tables numériques renferment un grand nombre de données intéressantes et chaque chapitre comporte une documentation bibliographique (p. ex. 99 références pour la chromatographie avec phase gazeuse). Impression et qualité des figures sont excellentes.

B. **Süsz** (Genève)

Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique, publiées sous la direction de J. A. **Gautier**. Cinquième série, Masson et Cie, Editeurs, Paris, 1957, 160 pp., Broché, 2100 frs.

La cinquième série de ces conférences annuelles faites à la Faculté de Pharmacie de Paris devant un auditoire nombreux, comme j'ai pu m'en assurer, nous apporte d'intéressantes mises au point dans des domaines très variés.

Le Prof. **Charlot** expose sommairement la théorie des deux modes de dosage coulométrique et le Prof. J. E. **Dubois**, après un rappel de l'étude des courbes de polarisation, traite de la polarovoltrie et de la polarométrie avec bibliographie choisie et récente. De son côté, R. **Pottier** étudie une demi-douzaine de dosages biologiques ou pharmacologiques utilisant curieusement des relations non-stoechiométriques (30 références). Les remarques de l'auteur sont tout à fait pertinentes. Les 3 conférences pratiques ont été prononcées par E. **André** sur les méthodes d'analyse des corps gras, par P. **Darmon** sur la recherche biologique des antiseptiques dans les vins et par P. **Dupaigne** sur l'analyse des jus de fruits avec bibliographie bien classée portant sur 621 titres.

J'ai déjà dit tout le bien que je pensais de cette intelligente collection fort bien présentée et qui ne représente pas une tentative sans lendemain puisque la sixième série a paru et que les conférences de la septième sont déjà exécutées. Ces mises au point servent de compléments précieux aux manuels de chimie analytique existants.

Cl. **Duval** (Paris)

THE RAPID ANALYSIS OF SILICATE ROCKS AND MINERALS

by

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Until recently practically the only methods available for the analysis of silicate rocks were the time-consuming classical methods described by Washington[1]. Collaborative tests using these procedures for the analysis of natural and synthetic silicates have revealed surprisingly large random errors for many elements and pronounced systematic errors for both silica and alumina[2-4].

Kvalheim[5] and Hegemann and Zoellner[6] have devised rapid spectrochemical methods for the determination of the common elements in silicate rocks. Their accuracy (at best *ca.* ±3%) is scarcely adequate for the determination of the most abundant elements such as silicon, aluminium and iron, except for some technical purposes. On the other hand the spectrochemical method is at least as accurate as the chemical method for the alkalis and minor elements such as manganese and titanium[7].

Shapiro and Brannock[8,9] have developed rapid methods for the analysis of silicate rocks using spectrophotometric, titrimetric and flame photometric procedures. For all but two elements, their methods are direct and fairly specific. They claim that if analyses are carried out in duplicate the accuracy is similar to that of conventional methods of analysis and that the speed is about three times as great. Recently a number of rapid procedures for the partial or complete analysis of silicates have been described employing similar methods[10-14].

This paper describes procedures which have been in use in these laboratories for the past two years for the analysis of silicate rocks and minerals. They are based on Shapiro and Brannock's methods, which have been considerably modified to increase the accuracy without loss of speed. In certain determinations a considerable saving in time is effected by the use of a single solution reagent.

PROCEDURES USED

The following is a brief description of the procedures used. The analysis is carried out in four parts. (1) Silica, (2) Metal oxides and phosphorus pentoxide, (3) Ferrous oxide, (3) Water and carbon dioxide.

Determination of silica

The sample is decomposed by fusion with sodium hydroxide in a silver crucible in a muffle furnace at 800°. The residue is dissolved in water, acidified and diluted to volume. Silica is determined in the solution (Solution A) by the molybdenum blue method of Mullin and Riley[15] using metol as the reducing agent. The use of silver crucibles in place of nickel enables the fusion to be carried out more rapidly with less attention and yields much clearer solutions. It has been found that more reproducible results are obtained using metol as reductant instead of the 1-amino-2-naphthol-4-sulphonic acid used by SHAPIRO AND BRANNOCK.

Determination of metal oxides and phosphorus pentoxide

The rock sample (0.5 g) is evaporated with a mixture of hydrofluoric and perchloric acids. The residue left, after fuming to dryness to remove fluoride, is dissolved in dilute perchloric acid and diluted to 500 ml. This solution (Solution B) is used for the determination of TiO_2, Fe_2O_3, Al_2O_3, MnO, CaO, MgO, Na_2O, K_2O, P_2O_5. The use of perchloric acid in place of sulphuric acid in the decomposition of the sample has a number of advantages. (*i*) Since the residue normally dissolves in about 20 ml of water, 25 ml platinum crucibles may be used for the evaporation instead of the 100 ml crucibles used by SHAPIRO AND BRANNOCK, (*ii*) No difficulty is experienced in dissolving rocks rich in calcium, (*iii*) perchloric acid readily fumes away under an infra red heater without spattering, and leaves an almost neutral residue.

1. Titanium dioxide is determined spectrophotometrically using the yellow colour formed by hydrogen peroxide in the presence of sulphuric and phosphoric acids. Although this reagent is less sensitive than Tiron, which was used by SHAPIRO AND BRANNOCK, it is simpler to use, and is less subject to interference from other elements.

2. Total iron oxide is determined spectrophotometrically as the red ferrous-dipyridyl complex, formed by addition of a single solution containing hydroxylamine hydrochloride, 2,2'-dipyridyl, and sodium acetate. No other elements interfere.

3. Aluminium oxide is determined spectrophotometrically in solution B. Iron is complexed as the ferrous-dipyridyl complex and aluminium is extracted with a chloroform solution of 8-hydroxyquinoline. The optical density of the yellow solution of the aluminium complex is measured. A small correction is necessary for titanium, but none of the other normal major components of silicate rocks interfere. If large amounts of elements, such as copper and nickel, which are extracted at pH 5.0 by a chloroform solution of 8-hydroxyquinoline are present, they may be removed by a preliminary extraction with a chloroform solution of 8-hydroxyquinaldine[16].

4. Manganese oxide is determined spectrophotometrically as permanganate. The oxidation of manganese is carried out with persulphate, as described by NYDAHL[17], since it gives more consistent results than periodate with small amounts of manganese.

5. Calcium and magnesium oxides. Before the chelatometric estimation of calcium and magnesium is performed, most other metals, except the alkalis, must be removed. Generally this separation is effected by precipitation of the hydroxides of the interfering elements with ammonium hydroxide. If only a single precipitation is employed, calcium and magnesium tend to be carried down with the precipitate unless the pH is so low that some aluminium remains unprecipitated. The separation is much more efficiently accomplished by extraction of the interfering elements as their 8-hydroxyquinoline complexes with chloroform in a continuous extractor[18]. Manganese is not removed and a correction must be made for its presence.

The calcium in the extracted solution is titrated with ethylenediaminetetraacetic acid using calcein as indicator[19]. The titration gives a very sharp end-point when carried out in screened ultra-violet light. Total calcium + magnesium is determined by titration of the buffered extracted solution with ethylenediaminetetraacetic acid using Eriochrome Black T as indicator.

6. Sodium and potassium oxides. Interfering elements are removed from solution B by passing it through a column of the anion exchange resin Amberlite IRA-400 in its citrate form. Ammonium sulphate is added as a spectroscopic buffer and the alkalis are determined with a flame photometer.

7. Phosphorus pentoxide. The molybdivanadophosphoric acid method for the determination of phosphorus[20] used by SHAPIRO AND BRANNOCK has been replaced by a single reagent molybdenum blue method, which has approximately twenty times the sensitivity[21].

Determination of ferrous oxide

Ferrous iron is determined on a separate sample by the conventional procedure.

Determination of water and carbon dioxide

Water and carbon dioxide are determined simultaneously on a further 0.5-g sample by the method of RILEY[22].

Dispensing of solutions and reagents

Pipettes of small volume are used for dispensing the sample and standard solutions in certain determinations, and considerable care is necessary to pipette reproducible amounts. Pipettes coated internally with silicone can be used but do not give such reproducible results. The same pipette should be used for measuring both the standard and sample solutions. Tilt measures are used for dispensing reagents.

Spectrophotometry

In the work described below, a Unicam S.P. 500 spectrophotometer was used with matched 1- or 4-cm glass cells. However, any precision spectrophotometer covering the wavelength range 400–850 mμ should be equally satisfactory. The instrument should be set to 100% transmission with distilled water in the compensating cell. The cell length and volume of solution taken for a determination should be adjusted so as to obtain, if possible, optical density readings lying in the range 0.3–0.75. The optical density increments recorded below for each spectrophotometric determination should only be taken as an indication of the values to be expected since they will vary slightly from one instrument to another.

In determinations where measurements are not made at the wavelength of maximum absorption, (*e.g.* aluminium and titanium oxides), a constant spectrophotometer slit width should be used.

In order to increase the precision of the analysis spectrophotometric determinations should be made in duplicate, or in the case of silica in quadruplicate. The optical density of each solution should be measured several times and the readings averaged.

Flame photometry

In the present investigations an Eel flame photometer was employed. Gelatine filters were used to isolate the desired spectral lines (5890 Å and 5896 Å for sodium, and 7665 Å and 7699 Å for potassium).

PREPARATION OF SOLUTION A AND THE DETERMINATION OF SILICA

The rock sample is fused with sodium hydroxide and the resultant cake dissolved in water. Silica is then determined in the acidified solution by the molybdenum blue method of MULLIN AND RILEY[15].

Reagents

Sodium hydroxide pellets, which should be stored in a firmly closed polyethylene bottle.

Sulphuric acid, 2.5*N*. Dilute 70 ml of concentrated sulphuric acid to 1 l.

Acid molybdate solution. Dissolve, with shaking, 2 g of ammonium molybdate in *ca.* 70 ml of water, add 6 ml of concentrated hydrochloric acid, and dilute to 250 ml. The solution, which is colourless, should be stored in a Pyrex glass bottle, and rejected if it turns blue.

Oxalic acid (10% w/v). Dissolve 10 g of oxalic acid A.R. in water, dilute to 100 ml and filter if necessary.

Sulphuric acid 25% v/v.

Metol–sulphite reagent. Shake 5 g of metol (*p*-methylaminophenol sulphate) with *ca.* 230 ml of water, in which 3 g of anhydrous sodium sulphite has been dissolved. After solution is complete, dilute to 250 ml and filter through a Whatman No. 1 paper into a brown glass bottle.

Reducing solution. Mix 85 ml of metol–sulphite reagent with 50 ml of 10% oxalic acid, add, while cooling, 100 ml of 25% sulphuric acid and dilute to 250 ml. This solution should be freshly prepared each week.

Standard silica solution. Quartz crystals or transparent Vitreosil fused silica rods are convenient sources of high purity silica. Pound the sample in a percussion mortar to pass an 80 mesh sieve. Boil the powder with concentrated hydrochloric acid to remove iron and then wash with hot water by decantation until free from acid. Dry the resultant silica at red heat in a silica crucible. Test its purity by evaporation of 1 g with 30 ml of 40% hydrofluoric acid and 0.5 ml of concentrated sulphuric acid in a platinum crucible, heat to 900°. The weight of the residue, after deduction of the reagent blank, should not exceed 0.5 mg. Weigh out accurately 0.1000 g of pure silica into a 30-ml silver crucible, add 1.5 g of sodium hydroxide pellets. Place the closed crucible in a silica basin and introduce into a muffle furnace at 700–800° for 5 min. When cold, add *ca.* 20 ml of water and heat on the water bath to aid solution. Place 25 ml of 2.5*N* sulphuric acid and 200 ml of water in a 1-l graduated flask. Transfer the contents of the crucible to the graduated flask, using a polyethylene funnel, and thoroughly wash the crucible with distilled water, dilute to volume. This solution contains 0.1 mg SiO_2/ml.

Procedure

Preparation of solution A. Weigh out accurately about 0.1 g of the powdered rock sample into a 30-ml silver crucible, and add 1.5 g of sodium hydroxide. Place the covered crucible in a muffle furnace at 800–850° for 5 min. To the cold residue add 20 ml of water and warm on the water bath to assist the solution of the fused cake. Pour the contents of the crucible through a polyethylene funnel into a 1-l graduated flask containing *ca.* 200 ml of water and 20 ml of 2.5*N* sulphuric acid. Rinse the crucible and its lid several times with distilled water. Add 5 ml of 2.5*N* sulphuric acid and scour it thoroughly with a rubber policeman. Add the washings to the graduated flask. If the solution is pink owing to the presence of much manganese in the sample add a small crystal of ferrous sulphate to reduce the permanganate. Dilute to volume and mix thoroughly. The solution should be clear and free from insoluble matter. Carry out a blank fusion in the same manner, omitting the sample.

Nickel crucibles may be used for the sodium hydroxide fusions; they are, however, difficult to clean and have only a short life. If they are used, the fusion must be carried out over a bunsen burner at a dull red heat, since sodium hydroxide tends to creep out of the crucibles when they are heated in a muffle furnace. The crucible, after solution of the fused cake, should be washed with water alone and 25 ml of 2.5*N* sulphuric acid placed in the 1-l graduated flask.

Spectrophotometry. All graduated flasks must be cleaned before use by treatment overnight with a 1:1 mixture of concentrated nitric and sulphuric acids. They should then be rinsed several times with distilled water, and drained but on no account allowed to become dry.

Pipette 2 ml of solution A into a 100-ml graduated flask, add about 10–15 ml of water and then 10 ml of the acid molybdate reagent from a tilt measure. After 15 min add 15 ml of the reducing solution from a tilt measure. Dilute to 100 ml. Measure the optical density of the solution at 812 mμ in a 1-cm cell after at least 12 h. Carry out a blank determination on the fusion blank. Standardise the method using 2 ml of the standard silica solution; this amount of silica (0.2 mg as SiO_2) gives an optical density of *ca.* 0.745 (after deduction of reagent blank, *ca.* 0.004).

If the rock sample is known to contain less than 40% silica the volume of rock solution taken should be stepped up accordingly. A corresponding blank run must be made using the same volume of the fusion blank solution. It is still, of course, necessary to carry out a blank run with 2 ml of the fusion blank solution to correct the standardisation.

In order to increase the accuracy of the silica determination, both standards and determinations should be carried out in quadruplicate and the optical density of each solution measured at least three times. The percentage of silica is calculated from the average values.

References p. 428

Calculation

$$\% \text{ SiO}_2 \text{ in rock} = \frac{\text{Optical density of unknown}^* \times 20}{\text{Optical density of standard}^* \times \text{ml of unknown} \times \text{sample weight}}$$

PREPARATION OF SOLUTION B

Solution B is prepared by digestion of the rock sample with hydrofluoric and perchloric acids. It is used for the determination of $Fe_2O_3°$, Al_2O_3, TiO_2, MnO, CaO, MgO, Na_2O, K_2O and P_2O_5.

Reagents

Hydrofluoric acid, A.R., perchloric acid 60% A.R.

Procedure

Weigh out exactly 0.5 g of the sample into a 25-ml platinum crucible. Add from a safety pipette 4 ml of perchloric acid and from a polyethylene measuring cylinder 15 ml of hydrofluoric acid. Heat the covered crucible on the water bath overnight. On the following morning remove the lid of the crucible and evaporate the hydrofluoric acid on the water bath. When no further fumes of hydrofluoric acid are visible, place the crucible under a vitreosil infra red heater and heat until most of the perchloric acid is removed but do not allow to become completely dry. Add 2 ml of perchloric acid and repeat the evaporation. Add 4 ml of perchloric acid from a pipette and 15 ml of water. Heat the covered crucible on the water bath and stir occasionally with a platinum rod until the cake has dissolved. If it resists solution, transfer it quantitatively to a 150-ml transparent silica flask. Add water up to a total volume of 100 ml and boil until all has dissolved. Transfer the cold solution to a 500-ml graduated flask and dilute to volume. This is *solution B*. Prepare a reagent blank solution in the same manner, but omitting the sample; this is *solution C*. A fresh reagent blank solution should be prepared each time new batches of reagents are used.

It is advisable to carry out the determination of the alkali metals as soon as possible after the preparation of solution B, in order to reduce the possibility of contamination of the solution by alkalis from glass.

RESISTANT MINERALS

Certain minerals are not readily attacked by the method described above and remain behind as gritty particles in the crucible after the cake has been dissolved. If the presence of such minerals is expected it is helpful to grind the rock sample to pass a 140-mesh sieve. The resistant minerals are of two types: the oxide minerals such as corundum, rutile and spinel, and silicate minerals such as tourmaline and staurolite.

(*a*) *Solution of rocks containing resistant oxide minerals*

In this method it is assumed that the alkali metals are entirely extracted when the rock is attacked with hydrofluoric and perchloric acids.

Carry out the evaporation with hydrofluoric and perchloric acids and solution of the cake as described above. Quantitatively transfer the contents of the crucible to a centrifuge tube, and centrifuge the oxide minerals down. Pour off the supernatant liquid into a 250-ml graduated flask. Wash the residue in the centrifuge tube several times with distilled water, centrifuge each time, and add the washings to the 250-ml graduated flask. Make the latter up to volume. This is *solution* B_1. Wash the oxide minerals back into the platinum crucible with a jet of water. Place the crucible under the infra red heater and evaporate the water. Add 0.50 g of fused potassium pyrosulphate A.R. (weighed to the nearest 0.02 g). Cover the crucible and heat it over a low gas until the pyrosulphate is molten and maintain it at this temperature for 10 min, then raise to a dull red heat for 3 min. To the cold crucible add 1 ml of perchloric acid and 15 ml of water. Warm on the water bath and stir until a clear solution is obtained. Transfer to a 250-ml graduated flask and make up to volume. This is *solution B_2*. Pipette 200 ml each of solutions B_1 and B_2 into a dry, stoppered flask, mix well. The resultant solution is used for the determination of all the elements which are normally determined in solution B, with the exception of the alkalis. The latter are determined in solution B_1. In calculation of the results for the alkalis it must be noted that the solution was made up to 250 ml and not 500 ml.

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* less corresponding reagent blank.

(*b*) *Solution of rocks containing resistant silicate minerals*

The decomposition of certain silicate minerals is a matter of considerable difficulty, two avenues of approach are open. In both cases it is helpful to first remove the more readily attacked minerals with hydrofluoric and perchloric acids, and to separate the unattacked residue by centrifugation, as described in section (*a*) above.

(*i*) If the alkali metal content of the resistant minerals is known to be negligible transfer the residue from the centrifuge tube to a 10-ml silver crucible using a jet of water. Evaporate the water under the infra red heater. Add 1 g of sodium hydroxide, place the covered crucible in a silica basin and introduce both into a muffle furnace at 750°. After 15 min allow the crucible to cool, add 5 ml of water and then heat on the water bath until the cake is thoroughly disintegrated. Transfer the residue and solution quantitatively to a platinum basin and evaporate to small bulk, add 4 ml of perchloric acid and 10 ml of hydrofluoric acid, and evaporate on the water bath. Heat under the infra red heater until the perchloric acid has almost evaporated. Dissolve the residue in 30 ml of distilled water containing 1 ml of perchloric acid, and dilute to 250 ml. This corresponds to solution B_2 of section (*a*) above.

(*ii*) If the resistant minerals contain alkali metals it is not necessary to dilute solution B_1 to 250 ml. Transfer the residue from the centrifuge to a bomb of polytetrafluoroethylene (Teflon); add 5 ml of hydrofluoric acid and 1 ml of perchloric acid. Put the tightly closed bomb inside a steel outer vessel, fitted with safety valves, which is ¼ full of water, screw its lid down tightly. Heat it in an oil bath fitted with a reliable thermostat at 150° for 3–4 h. When the apparatus has cooled, unscrew the lid of the pressure vessel and remove the Teflon bomb. Rinse the contents of the bomb into a platinum basin, add 1 ml of perchloric acid and evaporate on the water bath. Fume off most of the perchloric acid under the infra red heater. Add 1 ml of perchloric acid and 20 ml of water, warm on the water bath to complete solution and then add to solution B_1. Dilute to 500 ml and use this solution for all determinations except silica and ferrous iron.

DETERMINATION OF TITANIUM DIOXIDE

Titanium is determined photometrically in solution B by means of the yellow compound formed by the addition of hydrogen peroxide to the acid solution. Interference by iron is suppressed with phosphoric acid.

Reagents

Hydrogen peroxide reagent. Mix 200 ml of 50% v/v sulphuric acid, 200 ml of syrupy phosphoric acid and 200 ml of 30% (100 volume) hydrogen peroxide. Dilute to 1000 ml with distilled water. Store the reagent in an amber glass bottle closed with a loosely fitting glass stopper; it is stable indefinitely.

Standard titanium solution. Either "Specpure" titanium dioxide, or an analysed sample of anatase may be used as a standard for titanium. Weigh into a platinum crucible 0.1000 g of pure titanium dioxide, or a corresponding weight of anatase, and add 2 g of fused potassium pyrosulphate. Heat the covered crucible gently to remove water and then to dull redness for 15 min. Place the cold crucible in a 100-ml beaker containing 50 ml of 50% v/v sulphuric acid and simmer on the hot plate until the fused cake has dissolved. Dilute to 1 l. This solution contains 100 µg TiO_2/ml.

Procedure

Pipette 40 ml of solution B into a 50-ml graduated flask, make up to volume with hydrogen peroxide reagent, and mix thoroughly. Measure the optical density of the resultant solution at 400 mµ in a 4-cm cell; the yellow colour is stable indefinitely. Determine the reagent blank using 40 ml of the blank solution C. Standardise the method in the same fashion using 8 ml of the standard titanium solution. With fresh batches of reagents, distilled water blanks should also be run. They will normally be found to give the same value as solution C. 800 µg of TiO_2 gives an optical density of *ca.* 0.565 at 400 mµ in a 4-cm cell (reagent blank (*ca.* 0.012) deducted).

Calculation

$$\% \ \mathrm{TiO_2} \text{ in rock} = \frac{\text{Optical density of unknown}^{*} \times 2}{\text{Optical density of } 800 \ \mu\mathrm{g} \ \mathrm{TiO_2}^{*}}$$

DETERMINATION OF ALUMINA

Aluminium is determined photometrically in solution B. It is extracted with a solution of 8-hydroxyquinoline in chloroform, after adjusting the pH to 5, and complexing iron as the ferrous–dipyridyl complex. The absorption of the aluminium complex is measured at 410 mμ. A small correction is necessary for interference by titanium. Manganese does not interfere. Beryllium sulphate is added to complex any traces of fluoride remaining. In order to obtain the best results it is important to obey the instructions closely. In particular, it is essential that the pH of the solution before extraction should lie in the range 4.9–5.0.

Reagents

Hydroxylamine hydrochloride 25% w/v.

Sodium acetate (0.5*N*). Dissolve 17.0 g of hydrated sodium acetate in water, and dilute to 250 ml.

Dipyridyl solution. Dissolve 0.2 g of 2,2′-dipyridyl in 100 ml of 0.2*N* hydrochloric acid.

Beryllium sulphate. Dissolve 4 g of beryllium sulphate tetrahydrate in water and dilute to 100 ml.

Complexing reagent. Mix 4 ml of hydroxylamine hydrochloride solution, 50 ml of 0.5*N* sodium acetate, 20 ml of dipyridyl solution and 10 ml of beryllium sulphate reagent. Dilute to 100 ml.

8-hydroxyquinoline reagent (oxine). Dissolve 1.25 g of 8-hydroxyquinoline A.R. in 250 ml of chloroform B.P. Store the solution in an amber glass bottle in a refrigerator. Reject it if it becomes coloured.

Chloroform B.P.

Standard aluminium solution. Dissolve 0.0529 g of "Specpure" aluminium (99.99% Al) in a slight excess of dilute hydrochloric acid and dilute to 1 l. This solution contains the equivalent of 100 μg Al_2O_3/ml. Alternatively the standard solution may be prepared by dissolving 0.8894 g of ammonium alum A.R. in water and diluting to 1 l.

Procedure

Place 10 ml of water in a 50-ml stoppered separating funnel, add from a pipette 1 ml of solution B (0.5 ml if the rock contains over 20% Al_2O_3) and add 10 ml of the complexing reagent from a tilt measure. After 5 min add from a measuring cylinder 20 ml of 8-hydroxyquinoline reagent. Tightly stopper the separating funnel and shake it mechanically for 5–8 min. Run the chloroform layer through a small plug of filter paper (held in the stem of a 2.5-cm funnel) into a dry 25-ml graduated flask. Pour 2 or 3 ml of chloroform into the separating funnel and rotate it gently before allowing the chloroform to pass through the funnel into the flask. Make up to 25 ml with chloroform. Measure the optical density of the solution at 410 mμ in a covered 1-cm cell against chloroform in the compensating cell. Carry out a blank determination in the same fashion on an appropriate volume of the platinum blank solution C. Standardise the method by carrying out a determination on the platinum blank solution C to which 1 ml of the standard aluminium solution has been added. 100 μg Al_2O_3 give an optical density of 0.394, after deduction of the reagent blank (*ca.* 0.014).

Since the aluminium oxinate solutions are somewhat light-sensitive they should be kept in a dark cupboard until they are measured. For the same reason, the extractions should not be carried out in strong sunlight.

Used chloroform should be bulked for recovery and then treated as described on p. 422. Care should be taken not to mix this chloroform with that containing acetone, which has been used in the determination of calcium and magnesium.

Calculation

Correction for interference by titanium.

Let: corrected optical density of oxinate solution = D, observed optical density solution = D_0**, then $D = D_0 -$ (vol. of solution B × % TiO_2 in sample × 0.0106).

$$\% \ \mathrm{Al_2O_3} \text{ in rock} = \frac{10 \times D}{\text{optical density of } 100 \ \mu\mathrm{g} \ \mathrm{Al_2O_3} \text{ standard}^{**} \times \text{vol. of solution B.}}$$

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* after deduction of reagent blank. ** less corresponding reagent blank.

Note. The colour of the oxine extract should be pure yellow. If the extract shows any trace of green, iron is being extracted owing to pH of the aqueous solution being too low for the iron to be reduced to the ferrous state by the hydroxylamine. Such determinations should be repeated using sufficient buffer to bring the solution to the correct pH (4.9–5.0).

DETERMINATION OF TOTAL IRON OXIDE

Total iron is determined spectrophotometrically in solution B. Iron is reduced with hydroxylamine at pH 4.8–5.0 and complexed as the red ferrous–dipyridyl complex.

Reagents

Colour developing reagent.

(*a*) Hydroxylamine hydrochloride 25% w/v.

(*b*) Sodium acetate 0.5*N* (17.0 g of the hydrated salt/250 ml).

(*c*) Dipyridyl solution: dissolve 0.2 g of 2,2′-dipyridyl in 100 ml of 0.2*N* hydrochloric acid.

Mix 4 ml of hydroxylamine hydrochloride solution, 50 ml of 0.5*N* sodium acetate and 20 ml of dipyridyl solution. Dilute to 100 ml. The reagent is stable for at least 1 month.

Standard iron solution. Weigh out 0.1398 g of "Specpure" iron sponge, dissolve in 5 ml of 2*N* hydrochloric acid, and dilute to 2 l. This solution contains the equivalent of 100 μg Fe_2O_3/ml. Ferrous ammonium sulphate may also be used for the preparation of the standard iron solution, but is less satisfactory.

Procedure

Into a 50-ml graduated flask pipette 2 ml of solution B; this volume is suitable for rocks containing 7–20% Fe_2O_3. For Fe_2O_3 concentrations lying outside this range the volume of solution taken should be adjusted accordingly. Add from a tilt measure 5 ml of the colour developing reagent and then dilute to volume. Measure the optical density of the resultant solution in a 1-cm cell at 522 mμ. Carry out a blank determination on an appropriate volume of solution C. Standardise the method with 2 ml of the standard iron solution (200 μg Fe_2O_3). Carry out a reagent blank using only distilled water and the colour developing reagent. The red colour of the ferrous–dipyridyl is extremely stable, and measurements may be made up to 30 h after adding the dipyridyl reagent if the solutions are kept out of direct sunlight. Beer's law is obeyed up to at least 500 μg Fe_2O_3. 200 μg Fe_2O_3 give an optical density (less reagent blank *ca.* 0.010) of *ca.* 0.430 at 522 mμ in a 1-cm cell.

Calculation

$$\%\ Fe_2O_3 = \frac{\text{Optical density of sample}^* \times 20}{\text{Optical density of 200 μg } Fe_2O_3 \text{ standard}^* \times \text{volume of solution B}}$$

DETERMINATION OF MANGANESE

Manganese is determined spectrophotometrically in solution B by oxidation to permanganate by means of ammonium persulphate in the presence of phosphoric acid and a catalytic amount of silver ion.

Reagents

Acid reagent. Dissolve 37.5 g mercuric sulphate in 200 ml of concentrated nitric acid and 100 ml of water. Add 100 ml of 85% phosphoric acid and 0.017 g silver nitrate. Dilute the cold solution to 500 ml with water.

Ammonium persulphate A.R.

Standard manganese solution. Dissolve 0.0774 g of "Specpure" manganese in 20 ml of 0.5*N* sulphuric acid and dilute the cooled solution to 2 l. This solution contains the equivalent of 50 μg MnO/ml. Although the "Specpure" manganese is covered with a layer of oxide this is not sufficiently thick to cause any appreciable error in the strength of the manganese standard.

Procedure

Pipette 20 ml of solution B into a 50-ml conical flask, add 1.5 ml of the acid reagent and *ca.* 0.5 g of ammonium persulphate. Place the flask on the hot-plate (at a surface temperature of 400°) and boil for 1 min, not longer. Cool the flask under the tap and dilute its contents to 50 ml. Determine the optical density of the solution at 525 mμ (or at 575 mμ if much chromium is present). The permanganate colour is stable for at least 24 h. Determine the reagent blank using 20 ml of solution C; this determination need only be repeated when fresh batches of reagents are used. Calibrate the method using 2 ml of the standard manganese solution, run a corresponding blank with distilled water. 100 μg MnO give an optical density (less reagent blank *ca.* 0.002) of *ca.* 0.265 at 525 mμ in a 4-cm cell.

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* less corresponding reagent blank.

Calculation

$$\%\ \text{MnO} = \frac{\text{Optical density of sample}^{*} \times 0.5}{\text{Optical density of } 100\ \mu\text{g MnO standard}^{*}}$$

Note. Do not use a polyethylene wash bottle for making the solutions up to volume or fading of the colour may occur.

DETERMINATION OF CALCIUM AND MAGNESIUM OXIDES

Calcium and magnesium oxides are determined on solution B by titration with ethylenediaminetetraacetic acid after removal of interfering elements, except manganese, by extraction of their oxinates at pH 4.9–5.1 with chloroform in a continuous extractor. Manganese causes slight interference in the magnesium titration, and correction must be made for its presence.

Reagents

8-hydroxyquinoline. Dissolve 20 g of 8-hydroxyquinoline in acetone and dilute to 100 ml.

Sodium acetate. Dissolve 272 g of hydrated sodium acetate in water and dilute to 1 l.

Chloroform B.P.

For titration of calcium. Ethylenediaminetetraacetic acid (Versene). Weigh out 2.50 g of ethylenediaminetetraacetic acid (disodium salt) and 0.1 g of hydrated magnesium chloride. Dissolve in water, add 1 ml of calcein indicator and dilute to 2 l.

Sodium hydroxide 10% w/v. Store in a polyethylene bottle.

Calcein indicator. The indicator may be obtained from G.F. Smith Chemical Company, Columbus, Ohio, U.S.A., but is not available in the United Kingdom.

Preparation of calcein[19]. Mix together 5 g of fluorescein, 15 ml of ethyl alcohol and 7.5 ml of water, add 4.5 ml of 30% sodium hydroxide. When all has dissolved add, with stirring, 4.35 g of iminodiacetic acid (obtainable from Hopkin and Williams Ltd., London) dissolved in 12 ml of 15% sodium hydroxide. Cool to 10° and add 3.7 ml of 37% formaldehyde solution while shaking vigorously. After all the formaldehyde has been added, heat to 60–70° for 6–7 h with stirring. Cool, dilute to 150 ml and acidify with 1 : 1 hydrochloric acid. Filter off the precipitate and wash it well with water. Dissolve it in 150 ml of water in which 6 g of hydrated sodium acetate has been dissolved. Reprecipitate with hydrochloric acid, filter off and wash with water. Extract the precipitate twice with 100 ml of ethyl alcohol, filter off and dry in vacuum.

Preparation of indicator solution. Dissolve 1 g of calcein in 12.5 ml of *N* sodium hydroxide, and dilute to 50 ml. Store in a brown glass bottle.

For titration of total calcium + magnesium. Ammonia–ammonium chloride buffer. Dissolve 70 g of ammonium chloride in 600 ml of ammonium hydroxide (s.g. 0.880), dilute to 1 l with water.

Ethylenediaminetetraacetic acid (Versene). Prepared as for titration of calcium, but omitting the 1 ml of calcein.

Eriochrome Black T indicator (E.B.T.). Dissolve about 0.1 g of E.B.T. in 50 ml of ethyl alcohol. This reagent is stable indefinitely.

Standard solutions. Calcium chloride solution. Weigh out accurately 0.8925 g of A.R. calcium carbonate (dried at 110°). Transfer to a 150-ml beaker. Cover with a clock glass. Add 50 ml of water and then dilute hydrochloric acid gradually until all the carbonate has dissolved. Transfer to a 1-l volumetric flask and dilute to volume. 1 ml of this solution is equivalent to 500 μg CaO.

Magnesium chloride solution. Weigh out accurately 0.3015 g of "Specpure" magnesium. Dissolve it in a few ml of dilute hydrochloric acid in a beaker and dilute to 2 l in a volumetric flask. 1 ml of this solution is equivalent to 250 μg MgO.

Procedure

Removal of interfering elements. The continuous extractor used in removal of interfering elements is shown in Fig. 1. Place 250 ml of chloroform in the flask F, and cover it with a layer of 50% v/v sulphuric acid to prevent entrainment of 8-hydroxyquinoline in the chloroform vapour. Place 50–75 ml of chloroform in the body of the extractor.

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* less corresponding reagent blank.

Pipette 200 ml of solution B into a 500-ml conical flask, add 20 ml of sodium acetate reagent; the resultant solution should be pH 4.9–5.1. If the pH of the solution is less than this add more $2M$ sodium acetate. Mix well. Add with shaking, 10 ml of 8-hydroxyquinoline reagent, and immediately transfer the solution to the body of the extractor. If much molybdenum or vanadium are present the solution should be filtered before extraction. Wash the flask and precipitate with water, and add the washings to the extractor. Dissolve any precipitate remaining in the flask in 10 ml of chloroform and again add this to the extractor. Extract the solution for $\frac{1}{2}$ h, when it should be colourless and clear. Any dark coloured droplets of chloroform adhering to the side of the extractor are of no consequence since they are removed in the separating funnel. Switch off the heating mantle and allow to cool. Pour the liquid in the extractor into a 500-ml separating funnel. Wash the extractor well with water and add the washings to the liquid in the separating funnel. Draw off the lower (chloroform) layer. Filter the aqueous layer through a Whatman No. 1 filter and catch the filtrate in a 500-ml graduated flask. Wash the separating funnel and filter paper, and then make the solution up to volume. The chloroform in the flask of the extractor will suffice for at least 5 extractions before it needs to be renewed. The spent chloroform should be bulked for recovery. It must not be mixed with the chloroform recovered from the determination of alumina. Insoluble matter should be

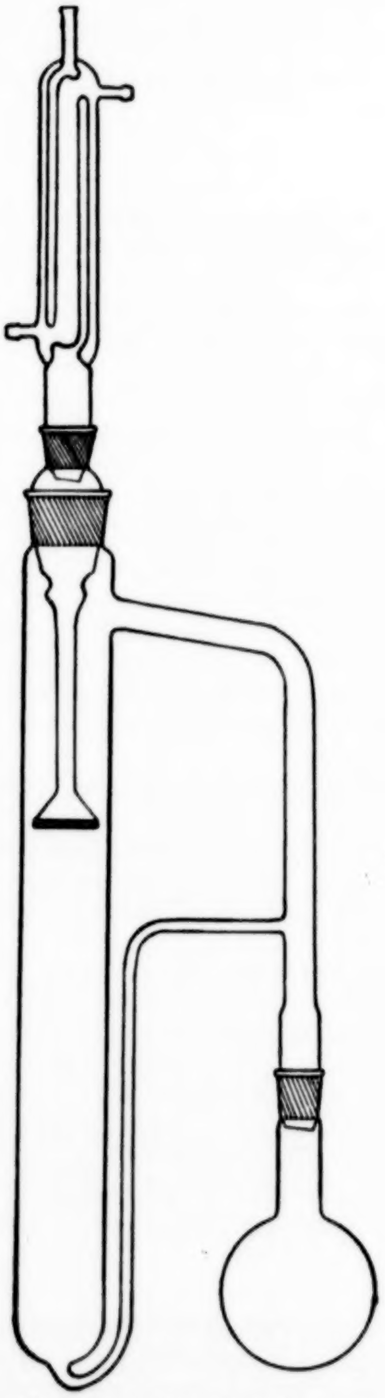

Fig. 1. Continuous extractor for removal of interfering elements in determination of calcium and magnesium.

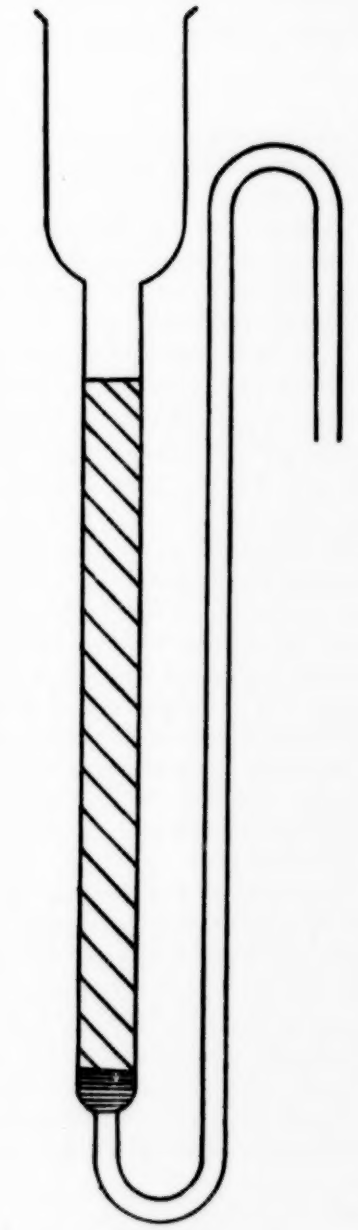

Fig. 2. Ion exchange column for use in determination of sodium and potassium.

filtered off, and the chloroform shaken with 10% sulphuric acid, and then distilled through a layer of 10% sodium sulphite. The distillate should then be shaken with 5% hydroxylamine hydrochloride solution and distilled from quicklime. About 1% by volume of ethyl alcohol should then be added as a preservative.

Note. A separating funnel may be used instead of the continuous extractor, but if much iron is present in the sample, emulsions may be formed which are slow to break.

Titration of calcium. Pipette 100 ml of the extracted solution B (50 ml if the rock sample contains over 10% CaO) into a porcelain evaporating basin, add 10 ml of 10% sodium hydroxide and 2–3 drops of calcein indicator. Titrate the solution with Versene containing calcein by the light of a screened ultra violet lamp in a darkened room. The onset of the end-point is indicated by a change in colour of the fluorescence of the solution from light yellow to a darkish brown. The versene should then be added dropwise with stirring after the addition of each drop. The titration is complete when no brown colour is formed where the drop enters the solution. The titration may also be carried out in daylight, when the colour change is from yellow to orange, but the end-point is not as sharp as when ultra violet light is used.

Titration of magnesium + calcium. Pipette 25 ml of the extracted solution B into a 500-ml beaker, add 300 ml of distilled water, 10 ml of ammonium hydroxide buffer, (if much manganese is present ($>0.5\%$) also add 5 ml of the same buffer which has been saturated with hydrogen sulphide), and 1.0 ml of E.B.T. indicator. Titrate the solution with versene solution to a clear blue-green colour, free from all traces of pink. The volumes of solution recommended for titration are suitable for rocks containing up to 10% of both CaO and MgO. If more is present the volumes should be reduced accordingly.

Reagent blank. Normally the reagent blanks for the method are negligible but they should be checked with each fresh batch of reagents.

Calibration. During the extraction a small amount of the aqueous solution becomes entrained with the chloroform (*ca.* 1.2%). It is therefore necessary to carry out the standardisation of the versene solutions with calcium and magnesium solutions which have been extracted.

Carry out extractions on distilled water containing 50 ml of the standard calcium solution and on distilled water containing 100 ml of standard magnesium solution, as described above. Titrate 100-ml portions of the extracted magnesium and calcium solutions with versene using E.B.T as indicator. Titrate 100-ml portions of the extracted calcium solution with the calcein containing versene solution, using calcein as indicator.

The versene solutions maintain their strength if kept in the dark and do not require standardisation more frequently than once a month.

Calculation

Let the titre of 100 ml of extracted standard calcium solution using calcein be T_1
100 ml of extracted standard calcium solution using E.B.T. be T_2
100 ml of extracted standard magnesium using E.B.T. be T_3
V_1 ml of extracted solution B using calcein be S_1
V_2 ml of extracted solution B using E.B.T be S_2

$\therefore$ 1 ml of calcein containing versene $\equiv \dfrac{5}{T_1}$ mg CaO

$$\%\ \text{CaO in rock} = \frac{1250 \times S_1}{T_1 \times V_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

1 ml of versene solution for CaO titration $\equiv \dfrac{T_2}{T_1}$ ml of versene in E.B.T titration.

Let the volume of versene equivalent to the calcium in solution B in the titration with E.B.T

$$V = \frac{T_2 \times S_1 \times V_2}{T_1 \times 100} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

1% of MnO in a rock requires 0.38 ml of versene solution for its titration in the magnesium titration if a volume of 25 ml of the extracted solution is taken. The following correction factor is thus applied to the volume S_2 found in this calculation.

$$\text{Corrected titre} = S_3 = S_2 - \frac{0.38 \times \%\ \text{MnO in rock} \times \text{vol. of extd. soln.}}{25}$$

Then, the volume of versene equivalent to the MgO in V_2 ml of solution B $= S_3 - V$.

$$\%\ \text{MgO in rock sample} = \frac{(S_3 - V) \cdot 1250}{T_3 \cdot V_2} \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

If 100 ml and 50 ml of extracted solution B are taken for the calcein and E.B.T titrations respectively the above equations simplify to:

$$\text{Eqn. (1) } \% \text{ CaO} = \frac{12.5 \cdot S_1}{T_1}$$

$$\text{Eqn. (2) } V = \frac{T_2 \cdot S_1}{T_1 \cdot 2}$$

$$S_3 = S_2 - 0.76 \times \% \text{ MnO in rock}$$

$$\text{Eqn. (3) } \% \text{ MgO} = \frac{(S_3 - V)}{T_3} \cdot 25$$

DETERMINATION OF SODIUM AND POTASSIUM OXIDES

After removal of iron, aluminium and titanium, by means of an anion exchange resin in its citrate form, the alkali metals are determined in solution B by means of an Eel flame photometer, using ammonium sulphate as a spectroscopic buffer. The determination should be carried out as soon as possible after the preparation of solution B, in order to minimise contamination of the solution by alkali from the glass of the flasks used.

Reagents

Citrate resin. Shake about 200 g of Amberlite IRA-400 (Cl) anion exchange resin (analytical grade) for 20 min with 400 ml of 10% citric acid solution. Allow to stand overnight, pour off the aqueous layer and repeat the shaking with a further 400 ml of 10% citric acid. Wash the resin well with distilled water, and store it in the moist condition.

Preparation of columns. The columns used are shown diagrammatically in Fig. 2; in use they are fitted in a rack by means of Terry clips. Fill the columns with water and then pour in a fine slurry of the citrate resin, until the top of the settled resin is *ca.* 1.5 cm above the tip of the siphon arms. Wash the columns with *ca.* 50 ml of water. Each filling of the columns should suffice for the treatment of 25 ml of solution B (assuming total $Fe_2O_3 + Al_2O_3$ does not exceed 20%). To regenerate the resin shake it several times with 1 *N* hydrochloric acid, and wash with water until the washings are practically free from acidity, and reconvert it to the citrate form as described above.

Ammonium sulphate solution 10% w/v.

Standard sodium solution. Prepare a solution containing 0.2291 g of anhydrous sodium sulphate per litre. This solution contains the equivalent of 100 µg Na_2O/ml. Prepare from it solutions containing 1, 2, 3, 4 and 5 µg Na_2O/ml, which also contain 40 ml of 10% ammonium sulphate per litre. Keep the solutions in tightly closed polyethylene bottles.

Standard potassium solution. Prepare a solution of potassium sulphate, containing 0.1850 g/l. This solution contains the equivalent of 100 µg K_2O/ml. Prepare from it solutions containing 40 ml of 10% ammonium sulphate per litre together with 1, 2, 3, 4 and 5 µg K_2O/ml. Keep these solutions in tightly closed polyethylene bottles.

Dilute ammonium sulphate solution. Dilute 40 ml of 10% ammonium sulphate solution to 1 l.

Procedure

Put 1 ml of 10% ammonium sulphate solution into a 25-ml graduated flask, and place the latter under the siphon tube of the ion exchange column. Pipette 2.5 ml of solution B (5 ml if the rock is low in alkali (< 1% Na_2O or K_2O)), into the top of the column. Allow it to percolate through, wash the column repeatedly with small (*ca.* 5-ml) portions of distilled water until the 25-ml flask is almost filled to the mark, remove the latter and complete to volume. Run a blank determination in the same manner using 2.5 (or 5 ml) of solution C.

Calibration of flame photometer. Prepare the flame photometer according to the manufacturer's instructions, introduce the appropriate filter. Set the zero of the instrument using the dilute ammonium sulphate solution instead of distilled water. Then set the galvanometer to give a full scale deflection with the appropriate strength of standard alkali metal solution (3 µg Na_2O or K_2O/ml if less than 4% of each is present in the rock, 5 µg Na_2O or K_2O/ml if 4–6% of each is present). Prepare a calibration curve for each alkali using the standard solutions and the appropriate filter. Since the potassium filter also transmits a small amount of sodium light it is necessary to prepare a calibration curve with standard sodium solution using the potassium filter, so that its interference may be allowed for. The calibration curve for potassium is a straight line, but that for sodium is slightly convex. Since the flame photometer often shows a small amount of drift the full scale deflection should be checked after each measurement; if this is found to have changed, the measurement should be repeated. Each standard solution should be measured four or five times and the readings averaged. Provided that the flame photometer is set each time it is used to a full scale deflection with the appropriate standard solution, the calibration curve will remain valid for some weeks, but should be checked periodically.

Measurement of solutions. Set the flame photometer to zero using the sodium filter and the dilute ammonium sulphate solution and to full scale deflection with the appropriate strength of standard sodium solution. Measure the galvanometer deflections of the reagent blank and of the sample solution. Each solution should be measured five times and the readings averaged. After each solution has been measured check the reading with the standard. Repeat the measurements using the potassium filter, setting the instrument to full scale deflection with the potassium standard. If the rock sample is very rich in sodium and potassium, and gives a solution which is too strong to measure, the solution should be diluted accordingly. It is not advisable to calibrate the instrument with strong solutions as this has been found to be less accurate.

Calculation

Determination of sodium. From the calibration curve determine the concentrations of sodium oxide (in μg/ml) corresponding to the scale readings of the reagent blank and of the sample solution. Then

$$\% \ Na_2O = \frac{(\mu g \ Na_2O/ml \text{ in sample} - \mu g \ Na_2O/ml \text{ in blank}) \times 2.5}{\text{Volume of solution B pipetted}}$$

Correction of potassium reading for interference by sodium. Find from the calibration curve the galvanometer readings which the determined concentration of sodium will give with the potassium filter; deduct this from the observed deflection given by the sample when this filter is used – this gives the corrected potassium scale reading.

Determination of potassium. Using the appropriate calibration curve read off the concentrations of potassium oxide (μg/ml) corresponding to the scale reading of the blank and the corrected potassium value.

$$\% \ K_2O = \frac{(\mu g \ K_2O/ml \text{ for corrected reading} - \mu g \ K_2O/ml \text{ in blank}) \times 2.5}{\text{Volume of solution B pipetted}}$$

DETERMINATION OF PHOSPHORUS PENTOXIDE

Phosphorus is determined in solution B by a single solution molybdenum blue method, using ascorbic acid as the reducing agent.

Reagents

Sulphuric acid, 3*N* (84 ml conc. sulphuric acid/l).

Ammonium molybdate. Dissolve 5 g of ammonium molybdate A.R. in water, dilute to 250 ml.

Ascorbic acid (0.1*M*). Dissolve 4.4 g of ascorbic acid in water, dilute to 250 ml. The solution should be stored in a refrigerator and made afresh if it becomes yellow.

Reducing solution. Mix 125 ml of 3*N* sulphuric acid, 38 ml of ammonium molybdate and 60 ml of ascorbic acid, dilute to 250 ml. The reagent, which is a faint green colour should be made up immediately before use.

Standard phosphate solution. Prepare a solution of potassium dihydrogen phosphate A.R. (dried at 110°), 0.959 g KH_2PO_4/l. This solution contains the equivalent of 50 μg P_2O_5/ml.

Treatment of flasks. To obtain accurate results all graduated flasks should be allowed to stand for several hours filled with concentrated sulphuric acid, and then washed well with distilled water. It is recommended that a set of graduated flasks be retained for use only in the determination of phosphorus. If the flasks are rinsed out after use and then kept filled with distilled water the acid treatment is only required occasionally.

Procedure

Pipette 25 ml of solution B into a 50-ml graduated flask, add 20 ml of the reducing solution and dilute to volume. After allowing to stand overnight, measure the optical density at 827 mμ in cells of an appropriate length (1 or 4 cm). Carry out a reagent blank determination on the platinum blank solution C. Standardise the method using 25 ml of distilled water, to which 1 ml (0.5 ml for

4-cm cell) of standard P_2O_5 solution has been added; carry out a corresponding blank using distilled water. 50 µg P_2O_5 in a final volume of 50 ml give an optical density (1-cm cell)of *ca.* 0.386, (after deduction of reagent blank *ca.* 0.008). The molybdenum blue colour is stable for at least a week.

Calculation

$$\% \ P_2O_5 \text{ in rock} = \frac{\text{optical density of sample}^* \times 0.2 \times \text{vol. of standard}}{\text{optical density of standard}^*}$$

DETERMINATION OF FERROUS OXIDE

Ferrous iron is determined by the classical method. The sample is attacked with a mixture of sulphuric and hydrofluoric acids, care being taken to avoid oxidation of the ferrous iron. Ferrous iron is then titrated with standard potassium dichromate solution using diphenylamine sulphonic acid as indicator. Certain silicate minerals, such as tourmaline, staurolite and axinite are only partly decomposed by the above procedure; they can be dissolved by fusing in an atmosphere of carbon dioxide with sodium metafluoborate in a Pyrex-tube[23].

DETERMINATION OF WATER AND CARBON DIOXIDE

Water and carbon dioxide are determined simultaneously by the method recently described by the author[22].

RESULTS

In order to test the proposed method samples of granite (G 1) from Westerly, Rhode Island, and of diabase (W 1) from Centerville, Virginia, were analysed in duplicate by 3 analysts. These rocks, which were obtained from the U.S. Geological Survey, were those used in the collaborative study reported by Fairbairn[2,3]. Tables I and II show that the results obtained agree well with those of earlier workers. Approximately 6–7 samples can be analysed in a normal 5½ day week. The same procedures have been successfully used for the analysis of rocks containing up to 80% calcium carbonate.

Work is proceeding on semi-micro methods for the analysis of silicate minerals.

ACKNOWLEDGEMENTS

The author thanks MR. S. K. EL WAKEEL AND MR. H. WILLIAMS for assistance with the analysis of W 1 and G 1, and MR. P. SINHASENI for Fig. 1.

SUMMARY

Methods are described for the rapid analysis of silicate rocks. They have an accuracy comparable with the best classical procedures but are about 5–6 times as rapid. The majority of the methods used are direct and specific. Silicon, titanium, total iron, aluminium, manganese and phosphorus are determined spectrophotometrically. Calcium and magnesium are estimated chelatometrically after the removal of interfering elements. Sodium and potassium are estimated using a flame photometer. Water and carbon dioxide are determined by the rapid method described by RILEY and ferrous iron by the conventional procedure.

Results, which are presented for the analysis of the standard diabase W 1 and granite G 1, show satisfactory agreement with the reported analyses. The methods have also been successfully used for the analysis of rocks containing up to 80% calcium carbonate.

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* less appropriate reagent blank.

TABLE I

ANALYSIS OF DIABASE W 1 (dried at 110°)

	Analyst 1		*Analyst 2*		*Analyst 3*		*Mean*	*Previous workers*	
	1	*2*	*1*	*2*	*1*	*2*		*a*	*b*
SiO_2	52.6	52.6	52.7	52.7	52.7	52.6	52.7	52.6	52.7
TiO_2	1.06	1.06	1.01	1.01	1.07	1.07	1.05	1.1	1.10
Al_2O_3	14.9	15.0	15.2	15.2	15.0	14.9	15.1	15.2	14.7
Fe_2O_3	1.37	1.40	1.66	1.55	1.69	1.66	1.56	1.4	1.5
FeO	8.80	8.82	8.50	8.50	8.60	8.67	8.65	8.7	8.7
MnO	0.17	0.18	0.17	0.17	0.17	0.18	0.17	0.16	0.17
CaO	10.79	10.77	10.78	10.87	10.82	10.81	10.8	10.9	11.0
MgO	6.67	6.65	6.65	6.70	6.64	6.67	6.7	6.6	6.6
Na_2O	2.25	2.25	2.26	2.25	2.18	2.19	2.2	2.1	2.0
K_2O	0.64	0.72	0.64	0.65	0.68	0.67	0.67	0.66	0.63
P_2O_5	0.13	0.12	0.14	0.14	0.13	0.14	0.13	0.15	0.13
H_2O+	0.60	0.59	0.58	0.61	0.58	0.60	0.60	0.59	0.62
Total	99.98	100.16	100.29	100.35	100.26	100.16	100.33	100.16	99.85

a. 5 analysts of U.S. Geological Survey quoted by SHAPIRO AND BRANNOCK[9]. b. FAIRBAIRN *et al.*[2], FAIRBAIRN AND SCHAIRER[3].

TABLE II

ANALYSIS OF GRANITE G 1 (dried at 110°)

	Analyst 1		*Analyst 2*	*Analyst 3*		*Mean*	*Previous workers*	
	1	*2*		*1*	*2*		*a*	*b*
SiO_2	72.7	72.7	72.5	72.7	72.6	72.6	72.5	72.9
TiO_2	0.26	0.25	0.22	0.24	0.24	0.24	0.25	0.25
Al_2O_3	14.0	14.0	14.3	14.0	14.1	14.1	14.3	13.9
Fe_2O_3	0.83	0.76	0.97	0.89	0.87	0.87	0.84	0.93
FeO	0.93	0.96	0.91	0.94	0.93	0.93	0.95	0.99
MnO	0.021	0.023	0.040	0.032	0.028	0.029	0.03	0.027
CaO	1.33	1.48	1.38	1.35	1.40	1.4	1.3	1.4
MgO	0.39	0.41	0.39	0.40	0.41	0.40	0.36	0.39
Na_2O	3.40	3.30	3.41	3.35	3.33	3.4	3.3	3.25
K_2O	5.50	5.40	5.33	5.58	5.60	5.5	5.5	5.40
P_2O_5	0.07	0.08	0.08	0.08	0.08	0.08	0.09	0.09
H_2O+	0.35	0.36	0.33	0.36	0.31	0.34	0.34	0.37
CO_2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.07	—
Total	99.78	99.72	99.86	99.92	99.90	99.89	99.83	99.90

a. 5 analysts of U.S. Geological Survey quoted by SHAPIRO AND BRANNOCK[9], p. 56. b. FAIRBAIRN *et al.*[2], FAIRBAIRN AND SCHAIRER[3].

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Received February 26th, 1958

THE DIETHYLDITHIOCARBAMATE OF TITANIUM

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According to MALISSA AND MILLER[1] and BODE[2], in their extensive work on the uses of diethyldithiocarbamate in analysis, titanium forms no complexes under the conditions examined, that is between pH 4 and pH 9.

In a recently developed method for the determination of aluminium in cast iron[3] separation of interfering elements is made by extraction of their diethyldithiocarbamates into chloroform; the aluminium is then extracted as cupferrate, and it was expected that any titanium in the iron would accompany the aluminium. Provision was made for a further separation if titanium cupferrate was observed, but during the course of analysis of a series of irons known to contain titanium, no such separation was found to be necessary. It seemed probable, therefore, that titanium was being separated in some way, and this was investigated. It was found that pure titanium solutions subjected to the normal procedure gave a bright yellow precipitate with sodium diethyldithiocarbamate in acetate - acid buffer solutions of pH 4.5 - 5.5, and in view of the lack of information in the literature on the subject, further investigations were made.

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Effect of pH

A series of solutions each containing 1 mg of titanium were adjusted to pH values increasing by one unit at a time from 0–10, using hydrochloric acid, acetic acid, sodium acetate and ammonium hydroxide to adjust the pH. (As sodium diethyldithiocarbamate is strongly hydrolysed in aqueous solution, the solutions were made up with sufficient buffer capacity to retain the pre-set pH values after the addition of the reagent). Precipitation of the titanium due to hydrolysis was seen to occur in the solutions of pH 6 and above. The solutions were transferred to separating funnels, the volume adjusted to 70–80 ml and 5 ml of a 1% aqueous solution of sodium diethyldithiocarbamate were added to each.

Yellow precipitates were obtained in the solutions with pH values 1–6 inclusive, with severe co-precipitation of white diethyldithiocarbamic acid in solutions of pH less than 5. The solutions were shaken for 1 min with 25 ml chloroform and the organic phase separated and evaporated to dryness. The organic residues were destroyed by fuming with nitric, perchloric and sulphuric acids, and the titanium in the extracts determined spectrophotometrically. Using the data thus obtained as a guide, the regions of pH of greatest interest were examined by the same procedure but at pH intervals of 0.25. The results are shown in Fig. 1, and indicate that for efficient extraction the pH is very critical and must be maintained as near 2.0 as possible. It is of interest to note that all the solutions mentioned earlier, in which titanium was not found, were extracted at pH 5.0–5.5, but were treated with several additions of diethyldithiocarbamate solution and extracted several times with chloroform in order to remove 0.1 g of iron(II) and other elements. As the extraction efficiency at this pH is only 50%, this would indicate that either complete extraction can be achieved at this pH in this way, or that the presence of a considerable excess (at least 1000 : 1) of other extractable ions will aid the extraction. We have not been able to increase the efficiency by repeated extraction, and conclude that the second explanation is more likely to be the correct one.

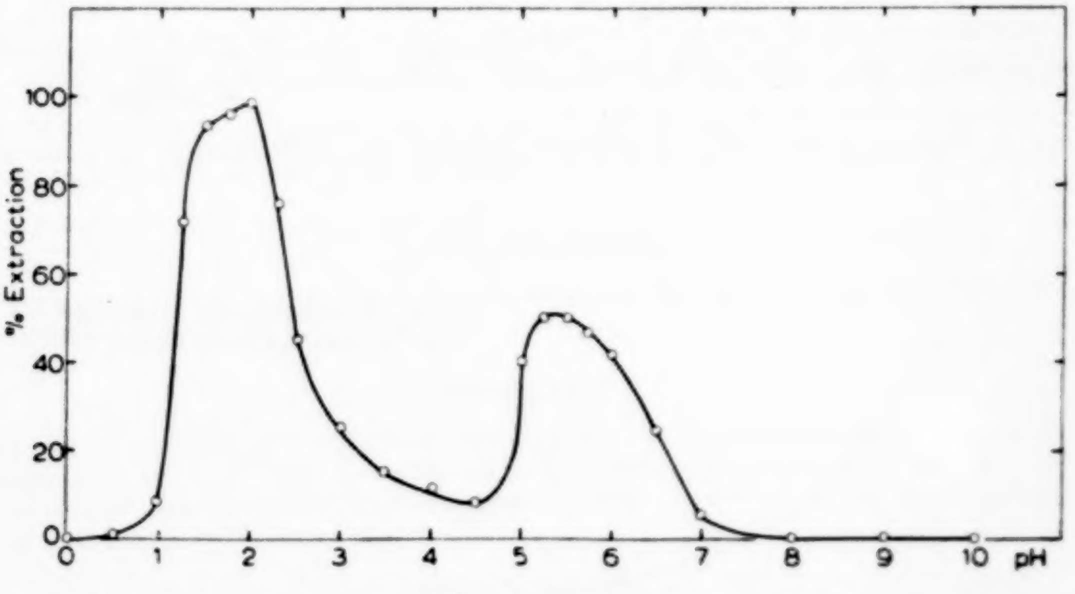

Fig. 1. Extraction of titanium diethyldithiocarbamate as a function of pH.

Interference

The effect of a number of anions at pH 2 was examined; it was found that sulphate, chloride, nitrate, acetate and perchlorate were without effect on the extraction. Oxalate, citrate, tartrate, phosphate and EDTA were all found to inhibit the extraction very strongly. In the presence of phosphate the titanium was precipitated on adjusting the pH to 2, and no extraction took place on subsequent addition of diethyldithiocarbamate and chloroform. As the reaction was inhibited at the pH of maximum efficiency, no work was done at other pH levels.

Spectrophotometry of the extract

1.0 mg of titanium(IV) was extracted at pH 2 into chloroform, and diluted to 25 ml. Absorption spectra of this solution and an extracted blank, *i.e.* a chloroform solution of diethyldithiocarbamic acid, were plotted using 1.0-cm fused silica cells and a Hilger "Uvispek" spectrophotometer. The curves are shown in Fig. 2, together with the difference between them.

These curves show that the colourless free acid solution shows considerable absorption in the ultra violet, becoming appreciable at wavelengths below 400 mμ. The yellow titanium complex

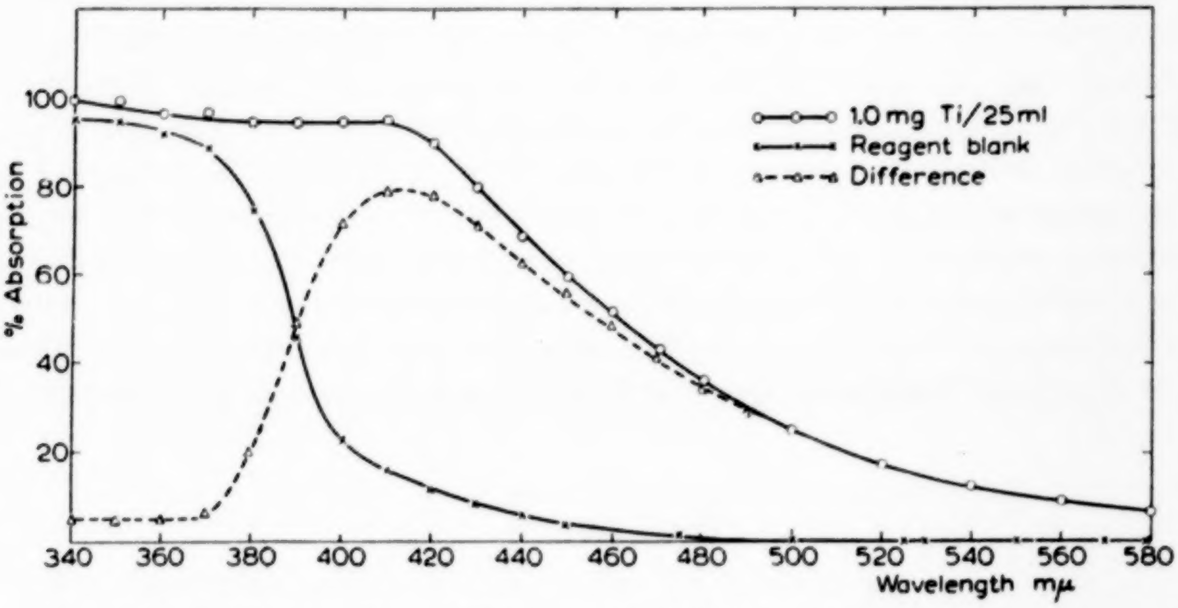

Fig. 2. Absorption spectrum of titanium diethyldithiocarbamate in chloroform.

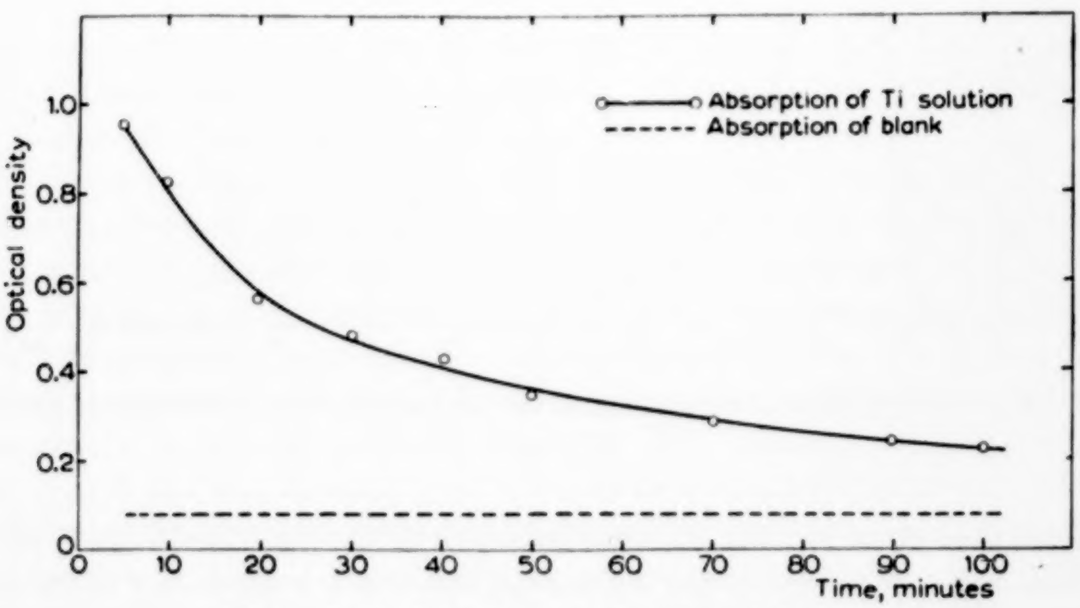

Fig. 3. Optical density as a function of time.

solution shows a band of continuously increasing absorption as the blue end of the spectrum is approached, the maximum difference occurring at 410–420 mμ. The sensitivity, using freshly prepared solutions was quite high, the "difference"-optical density being about 0.7 for 0.2 mg of titanium in 25 ml. This compares favourably with optical density 0.15, obtained for 0.2 mg of titanium using hydrogen peroxide as reagent under identical conditions as regards volume of solution and cell size, but measured at its maximum of 400 mμ.

Effect of standing time

The possibility of using this reaction to determine titanium was investigated in view of the apparent gain in sensitivity over hydrogen peroxide, but was found to be impracticable owing to the high degree of colour instability with time. A solution containing 0.2 mg of titanium was prepared and the optical density measured 5 min after the addition of the sodium diethyldithiocarbamate solution to the separating funnel. This was found to be the minimum time required for addition of reagents, extraction of the complex, dilution to volume and filtering the solution into the spectrophotometer cell. The optical density was measured again after a further 5 min, and thereafter at periods of 10 min. The decay curve is shown in Fig. 3. The constant absorption recorded for the blank would seem to indicate that the colour decay is not due to destruction of the complex due simply to instability of the diethyldithiocarbamic acid residue, but is a function of the titanium compound as such.

CONCLUSIONS

The yellow diethyldithiocarbamate complex of titanium can be extracted into chloroform from aqueous solutions of pH 2. The reaction is apparently not very suitable for the colorimetric determination of titanium owing to the instability of the colour, but can be used to separate titanium from other members of the analytical group III. Only iron and some uranium will accompany the titanium into the chloroform layer, and these can be further separated by ion exchange or solvent extraction. The main use, however, would appear to be the removal of titanium, together with many other elements, from solutions of aluminium, cerium, etc. before their subsequent determination. It is in this way, particularly in the field of trace element analysis, that the reaction is being used in our laboratories.

ACKNOWLEDGEMENT

The author wishes to thank the Director and Council of The British Cast Iron Research Association for permission to publish this work.

SUMMARY

The diethyldithiocarbamate complex of titanium has not been previously reported in the literature. Conditions for its formation and extraction have been examined, together with some interferences. An absorption spectrum has been plotted, and the possibility of determining titanium by means of this reaction investigated.

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Received April 8th, 1958

ANALYSE QUALITATIVE ET DÉTERMINATION COLORIMÉTRIQUE DU COBALT AU MOYEN DE LA CARBOXY-2-ISONITROSOACÉTANILIDE

par

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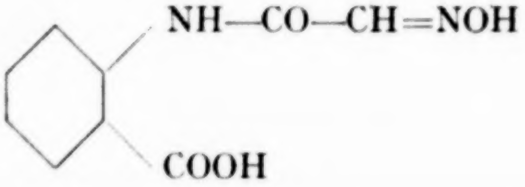
Dans la présente communication, les auteurs font l'exposé d'une nouvelle réaction pour l'analyse qualitative du cobalt et pour sa détermination colorimétrique, au moyen de la carboxy-2-isonitrosoacétanilide



ce réactif est étudié du point de vue de ses applications analytiques et les résultats seront communiqués dans nos prochaines publications.

En solution alcoolique, la carboxy-2-isonitrosoacétanilide donne avec le cobalt, en milieu ammoniacal, une coloration rouge-vineux; seul le nickel donne la même réaction. Ainsi, après traitement par un cyanure alcalin pour former un ion complexe avec le nickel, la méthode devient spécifique pour le cobalt, (Cu et Fe^{+2} donnant des colorations respectivement verdâtre et brune, beaucoup moins sensibles et également éliminables par un cyanure). La sensibilité de cet essai pour Co(II) est de $D = 10^{-6}$ (1:1,000,000).

Cette grande sensibilité, comparable à celles des réactifs les plus sensibles de cet

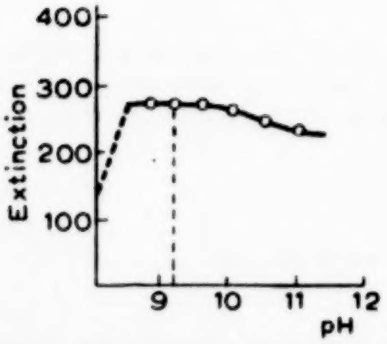


Fig. 1. Variation de l'extinction en fonction du pH à 420–465 mμ.

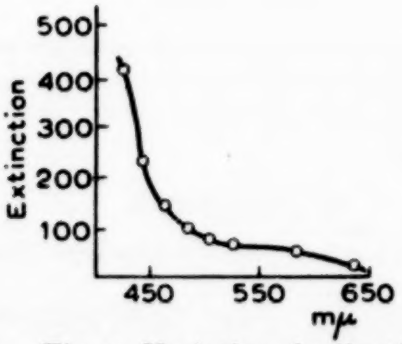


Fig. 2. Variation de l'extinction, à pH 9.2, avec la longueur d'onde.

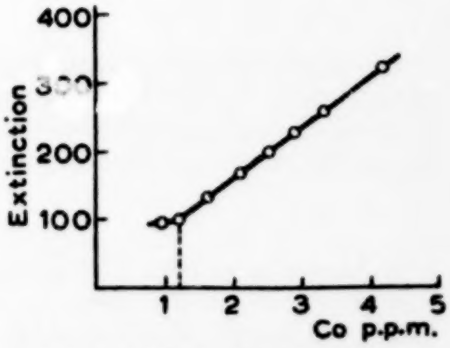


Fig. 3. Variation de l'extinction en fonction de la concentration de Co(II), à 420–465 mμ et pH 9.2.

élément, et le fait que la solution du réactif est incolore même en présence d'ammoniaque nous ont amené à l'étude de son application à la détermination colorimétrique du cobalt.

La Fig. 1 montre les variations de l'extinction entre 420 et 465 mμ en fonction du pH; on constate que le pH optimum est 8.5–9.5.

Les Figs. 2 et 3 montrent, pour un pH déterminé, les variations de l'extinction en fonction de la longueur d'onde et de la concentration. La loi de Beer se vérifie, même pour des solutions dont la teneur en cobalt est de 1.2 γ/ml (1.2:1,000,000).

La coloration des solutions se stabilise au bout de vingt minutes; elle se maintient en donnant des valeurs constantes pour l'extinction, pendant plus de trente minutes, ce qui constitue un espace de temps largement suffisant pour effectuer le dosage.

PARTIE EXPÉRIMENTALE

Reactifs

Nitrate de cobalt cristallisé (*Analytical grade*). La concentration de la solution a été déterminée d'après la méthode usuelle, en pesant le cobalt sous forme de $CoNH_4PO_4 \cdot H_2O$. La concentration en cobalt était de 2.6390 g/l. On a préparé par dilution une solution contenant 10.5 γ/ml.

Solution de carboxy-2-isonitrosoacétanilide P.F. 206–208°. 1 g dans 100 ml d'alcool, solution incolore.

Hydroxyde d'ammonium, 2N.

Appareillage

La courbe spectrale a été déterminée au moyen d'un spectrophotomètre Beckman mod. DU avec photomultiplicateur, et avec une cuve de 10 mm.

Les diverses déterminations colorimétriques ont été effectuées avec un photocolorimètre à filtres Engel, de la firme Kipp & Zonen travaillant avec une zone spectrale à transmission maxima à 430 mμ. Le photocolorimètre est muni d'un galvanomètre A 75 de la même marque et dont la sensibilité est de $3 \cdot 10^{-10}$ A/mm sur l'échelle.

Suivant la teneur en cobalt, les cuves utilisées ont des épaisseurs comprises entre 16 et 40 mm.

Détermination quantitative du cobalt

Au moyen d'une pipette, 20 ml d'une solution contenant 10.5 γ Co/ml, sont introduits dans un ballon jaugé de 25 ml. On ajoute 3 ml de la solution alcoolique de carboxy-2-isonitrosoacétanilide et finalement 0.25 ml de NH_4OH 2*N* au moyen d'une micropipette. On complète immédiatement jusqu'au trait de jauge avec de l'eau distillée.

Après 20 min, on effectue les lectures au photocolorimètre avec le filtre 43 (transmission maxima à 430 mμ).

Recherche qualitative du cobalt

Méthode. (Dans un microtube). À 1 ml de la solution contenant Co(II), on ajoute 0.5 ml de solution alcoolique de carboxy-2-isonitrosoacétanilide et 5 gouttes de NH_4OH 2*N*. Une coloration rouge-vineux apparaît immédiatement.

Sensibilité et spécificité. $D = 10^{-6}$ (1:1,000,000). Ni(II), Cu(II), et Fe(II) gênent, KCN permet de masquer Ni et Cu en formant des complexes. Quant à $Fe(OH)_2$ qui précipite, il peut être filtré du milieu ammoniacal dans lequel s'effectue la détermination. La réaction devient alors spécifique pour Co. La présence du complexe cyané de Ni n'altère pas la sensibilité de la réaction et le complexe cyané de Cu rend légèrement plus jaune la coloration du complexe du cobalt avec le réactif. En présence de grandes quantités de cuivre, il est donc préférable d'éliminer celui-ci par précipitation sous forme de sulfure.

RÉSUMÉ

Une nouvelle méthode est proposée pour l'identification et pour le dosage colorimétrique du cobalt, au moyen de la carboxy-2-isonitrosoacétanilide. Le réactif est spécifique et sa sensibilité est de $D = 10^{-6}$ (1 : 1,000,000). On indique les conditions optima pour le dosage colorimétrique; la loi de Beer se vérifie pour les dilutions allant jusqu'à 1.2 : 1,000,000.

SUMMARY

A new method for the identification and colorimetric estimation of Co(II) with 2-carboxy-isonitrosoacetanilide has been developed. This reagent is specific and its sensitiveness is $D = 10^{-6}$ (1 : 1,000,000). The best possible conditions are indicated for the colorimetric determination whereby Beer's law holds for dilutions up to 1.2 : 1,000,000.

Reçu le 24 mars 1958

IDENTIFICATION AND COLORIMETRIC DETERMINATION OF $Fe(CN)_6^{-3}$ ION WITH *o*-DIANISIDINE

by

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We have described previously some analytical applications of *o*-dianisidine[1,2].

In the present work an account is given of its application to the determination of ferricyanide ion, the aqueous solutions of which react with *o*-dianisidine to give an intense blue-green coloration that turns red on acidification.

A study of the best possible conditions for carrying out the colorimetric assay of this ion led us to draw the following conclusions:

(a) The absorption spectra (Fig. 1) show that the red colour obtained in an acid medium has a greater extinction than the blue ones, thus allowing determinations in more dilute solutions. The spectrum of the red solution thus obtained shows a maximum in the 460–480 mμ zone.

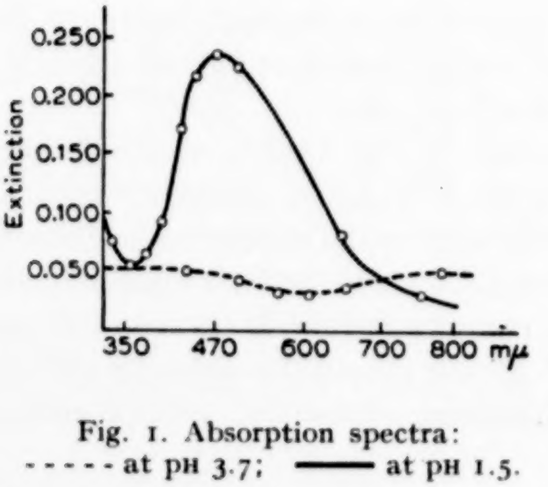

Fig. 1. Absorption spectra: - - - - - at pH 3.7; ——— at pH 1.5.

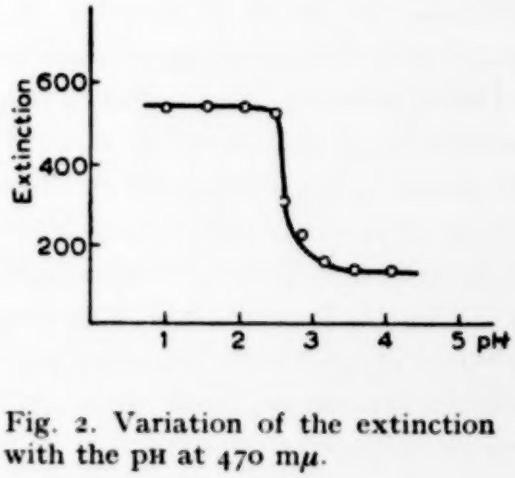

Fig. 2. Variation of the extinction with the pH at 470 mμ.

(b) The pH value has an influence, a green colour being produced at values above 2.8 and a red one below 2.8. Evidence has been obtained that in the horizontal part of the curve, the colour intensity does not depend on the acid used for acidification (Fig. 2).

(c) Colour intensity increases greatly when the reagent consists of a solution of *o*-dianisidine in aqueous acetone (prepared as described under EXPERIMENTAL) instead of the acetic solution used in our previous work. This modification increases the dilution limit from $1:10^6$ to $1:1.5 \cdot 10^6$.

(d) Both reagents yield a colour which takes 5 min to develop, after which the maximum intensity is reached and remains unchanged for 25 min.

Fig. 3 shows clearly that the colour obtained follows Beer's law in a wide interval from 1–10 mg/l, and Fig. 4 shows the variation of the extinction with the concentration of ferricyanide ion in the area near the dilution limit of $D = 10^{-6.3}$

In cases when perfect accuracy is not required, the ferricyanide content can also be determined with Nessler tubes, and we have checked that if these tubes have a useful thickness of 210 mm (according to the prescriptions of the American Health Association), quantities of ferricyanide from 5–25 γ in 25 ml can also be estimated. These intervals correspond to a dilution limit of $1:2.5 \cdot 10^6$ and $1:5 \cdot 10^6$.

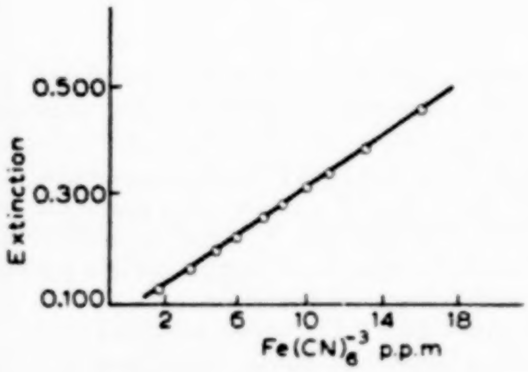

Fig. 3. Variation of the extinction with the $Fe(CN)_6^{-3}$ concentration, at 470 mμ and pH 1.5.

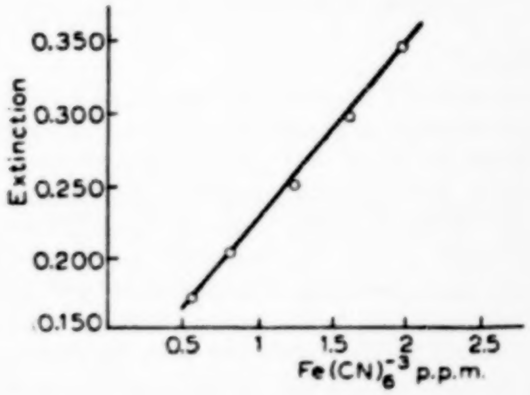

Fig. 4. Variation of the extinction in the dilution limit area, at 470 mμ and pH 1.5.

It must be pointed out, however, that the maximum intensity of the coloration thus obtained is maintained for 10 min only, after which it decreases appreciably.

In accordance with the statements made above, a method has been devised permitting the colorimetric estimation of ferricyanide ion. It is highly sensitive, simple and the reagent used is very easy to prepare. This method has the one inconvenience that other oxidizing agents accompanying ferricyanide may possibly interfere. As in similar cases, they must first be removed by suitable treatment of the sample.

The sensitivity of the reaction, $D = 10^{-6.7}$ $(1:5 \cdot 10^6)$, is higher than that of some reactions recommended for the estimation of ferricyanide ion: with benzidine acetate (1:10.000), phenolphthalein (1:60.000); it is even higher than that of the ferrous sulfate reaction which under similar conditions reaches $1:2.5 \cdot 10^6$, as we have verified[3].

In view of these advantages, we endeavoured to apply the method to the estimation of $Fe(CN)_6^{-3}$ in the presence of $Fe(CN)_6^{-4}$, I^-, CN^-, SCN^-, Cl^-, and Br^- ions, since these ions form the first group of anions in the classical analytical procedure. The research was successful not only in the case of solutions of sodium or potassium salts of the anions, but also when the estimations were made directly with the precipitate of the silver salts, a very intense red stain being obtained when the reagent was applied to the filter. When the I^- concentration is very high compared with that of $Fe(CN)_6^{-3}$ (over 1.000:1) the red colour developed in the solution vanishes after 10 min; if the reaction is carried out with precipitated silver salts, the coloration obtained has a much higher stability.

EXPERIMENTAL

Reagents

Potassium ferricyanide. Analytical grade. After being recrystallized many times from water and dried at 100°, it is considered as a standard substance[4]. A solution was prepared containing 1 g $Fe(CN)_6^{-3}$ per l, from which the solution used in the experiments, containing 0.1 g/l, was obtained by dilution (1 : 10).

Sulfuric acid 2N.

o-Dianisidine solution. 0.5 g *o*-dianisidine was dissolved in 50 ml of acetone and the volume made up to 100 ml with distilled water. The solution thus obtained is slightly coloured, but it can be safely used without further purification.

Acetone. Analytical grade.

Apparatus

The spectral curve was determined by means of a Beckman spectrophotometer Model DU with photomultiplier attachment, 10-mm cuvettes and the most appropriate slit width for maximum sensitivity.

For the various colorimetric determinations, an Engel filter-photocolorimeter (manufactured by Kipp & Zonen, Delft) was also used. Filter 47 with a spectral region of 430–505 mμ and a maximal transmission at 470 mμ was used, but good results were also obtained with Filter 45 (spectral region 430–480 mμ, maximal transmission 450 mμ). The photocolorimeter is equipped with a galvanometer A 75 of the same make, with a sensitivity of $3 \cdot 10^{-10}$ A/mm on the scale.

According to the absorption to be measured, the cells used had a thickness of 5–40 mm.

The pH measurements of the solutions were made with a Beckman Model G pH meter.

METHOD

Quantitative determination

The solution is delivered from a microburette to a 25-ml measuring flask, then 2 ml of $2N$ H_2SO_4 are added, followed by 2 ml of $2N$ $ZnSO_4$ and 2 ml of the reagent. The volume is made up to 25 ml with distilled water. The red solution thus obtained is poured into the cuvette of the spectrophotometer or the photocolorimeter; the extinction is then measured at 470 mμ. The readings must be made between 5 and 25 min after the colour has developed.

Qualitative investigation

Filter-paper method. One drop of the solution containing $Fe(CN)_6^{-3}$ is placed on filter-paper, followed by one drop of $2N$ H_2SO_4 and one drop of $2N$ $ZnSO_4$ and, finally, one drop of the reagent solution. A red stain develops. $D = 10^{-5.7}$.

Porcelain plate, micro and macro-test tubes. The reaction takes place similarly and with a sensitivity similar to those previously obtained. When the macro-tube is used, the sensitivity reaches $D = 10^{-6.3}$, as the greater the volume, the more clearly the colour is observed.

SUMMARY

A new method for the investigation and colorimetric determination of ferricyanide ions is described. The reagent used is a solution of *o*-dianisidine in aqueous acetone, which gives a red colour with $[Fe(CN)_6]^{-3}$ when the pH is 2.8. Beer's law is obeyed up to dilutions of $1 : 2 \cdot 10^6$ ($D = 10^{-6.3}$)

and, when 210-mm Nessler test-tubes are used, up to dilutions of $1:5\cdot10^6$ ($D = 10^{-6.7}$). The qualitative investigation gives good results even when ions of the first group of the usual analytical procedure for anions are present; the sensitivity is $1:1.5\cdot10^6$ ($D = 10^{-6.7}$).

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Received March 24th, 1958

NEW SPECIFIC TEST FOR CALCIUM

by

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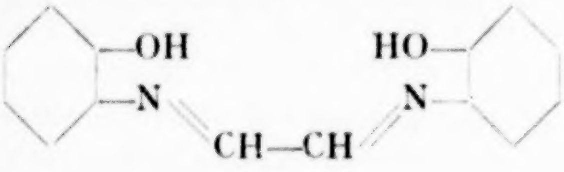
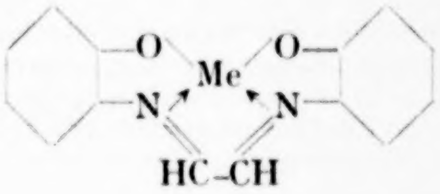
As stated recently by BAYER[1], glyoxal bis[2-hydroxy-anil], which is a Schiff base (I), forms coloured inner complex salts with copper, cobalt, nickel, cadmium, manganese and uranyl ions, with the general formula (II).



(I)



(II)

The respective salts were isolated as dihydrates by warming a methanolic solution of the corresponding acetates with a methanolic solution of (I).

It seemed interesting to investigate a possible application of the formation of the above-mentioned compounds and of those that could be formed with other metals. It was found that under certain conditions the Schiff base is a highly selective reagent for calcium ions. When its alcoholic solution is added to an aqueous solution of a calcium salt, followed by sodium hydroxide, a red precipitate is obtained. Barium and strontium salts show a similar behaviour, but curiously enough it was found that in the case of these two metals the coloured precipitates once formed are destroyed by addition of alkaline carbonate, whereas the calcium compound remains unaltered.

Aqueous solutions of the following ions were treated with the reagent plus sodium hydroxide and carbonate: aluminum, antimony, barium, beryllium, bismuth, cadmium, ceric, cesium, chromic, cobalt, copper, ferric, gold, lanthanum, lead, lithium, magnesium, manganese, mercurous, mercuric, nickel, palladium, platinum, potassium, silver, stannous, stannic, thallium, thorium, titanium, uranyl, zinc, and zirconium. Disregarding the hydroxide precipitates, of the above-mentioned ions only cobalt and nickel give a red precipitate, cadmium a violet one, and copper a dark coloured one.

When the suspension of the calcium-glyoxal bis[2-hydroxy-anil] compound is shaken with chloroform, the organic layer acquires a red colour. The copper, nickel and cobalt compounds do not behave like this, but the cadmium compound, when similarly treated gives a blue coloured chloroform layer. It seems that the coloured chloroform solution is really an organo-sol. An indication for this assumption is the fact that the dry coloured precipitate when treated with chloroform does not dissolve.

From the above it can be concluded that the reagent is fairly selective for calcium. Specificity can be attained by using a sodium hydroxide solution containing cyanide, thus preventing (masking) the cadmium reaction through the formation of $Cd(CN)_4^{-2}$ ions; in contrast, the calcium reaction is not affected by cyanide. It is convenient to follow the same procedure in the presence of large amounts of nickel, copper, and cobalt ions, which are likewise masked by the formation of complex cyanides. In this way the action of the reagent (which otherwise would also be consumed by these ions) is restricted to the calcium ions.

Although the composition of the calcium compound with glyoxal bis[2-hydroxy-anil] has not yet been investigated, it is probable that an inner complex salt with the general formula (II) is involved.

EXPERIMENTAL

Reagents

1. *Saturated solution of glyoxal bis[2-hydroxy-anil] in ethyl alcohol.* This solution is stable for at least two months, even though it may darken a little.

The reagent may be prepared according to BAYER[1], by dissolving 4.4 g of freshly sublimed *o*-aminophenol in 1 l water at 80° and adding 3.0 g of a 40% solution of glyoxal in water. The mixture is kept for 30 min at 80° and afterwards for 12 h in the refrigerator. The precipitate is filtered, washed with water and recrystallized from methanol.

2. *10% solution of sodium hydroxide.*
3. *10% solution of sodium carbonate.*
4. *10 g potassium cyanide and 10 g sodium hydroxide in 100 ml water.*
5. *Chloroform.*

Procedure

A drop of the neutral or acid test solution is treated successively in a micro test tube with 4 drops of the organic reagent (1), 1 drop of sodium hydroxide, 1 drop of sodium carbonate and extracted with 3–4 drops of chloroform. Addition of a few drops of water hastens the separation of the two layers. A red colour in the chloroform layer indicates the presence of calcium. When testing for small amounts of calcium, a blank test is advisable.

Limit of identification

0.05 γ calcium.

Limit of dilution

1:1,000,000.

With the above procedure it is possible to identify the following amounts of Ca:

Calcium	*In the presence of*	*Calcium*	*In the presence of*
20 μg	2000 μg strontium	1 μg	500 μg fluoride
25 μg	2000 μg barium	0.5 μg	500 μg oxalate
30 μg	1000 μg magnesium	5 μg	500 μg phosphate
20 μg	500 μg lead	0.5 μg	500 μg sulfate
10 μg	500 μg iron	0.5 μg	500 μg chromate
0.5 μg	500 μg aluminum		

In the presence of cadmium, copper, nickel, and cobalt salts, the procedure is the same as described above, but the alkalization should be performed with a sodium hydroxide solution containing cyanide (reagent 4).

References p. 439

In this way it is possible to identify:

Calcium	*In the presence of*
1 μg	1000 μg cadmium
0.5 μg	500 μg copper
1 μg	500 μg nickel
1 μg	500 μg cobalt

Distinction between calcium oxide and the oxides of barium, strontium and magnesium

It is possible to distinguish calcium oxide from barium, strontium and magnesium oxides without dissolving any of them. It is sufficient to treat the sample with the reagent solution. Only calcium oxide becomes red.

Procedure. A little of the finely powdered solid is treated on a spot plate with one drop of the reagent solution. After evaporation of the greater part of the solvent (by simply blowing through a pipette), the previously white solid will be tinted red if calcium oxide is present.

The procedure can also be applied to a carbonate mixture, after previous ignition of the sample.

Identification of calcium in pharmaceutical products

FEIGL AND SILVA[2] described a test for detecting calcium in pharmaceutical preparations using sodium rhodizonate and sodium hydroxide as reagents. Calcium lactophosphate fails to give a positive response to this test. With the first procedure described, the calcium present in this compound can be detected; a positive reaction is also shown by calcium pantothenate, "zalima" (containing 1% calcium formate), calcium lactate, calcium gluconate and calcium laevulinate.

Preliminary experiments showed that glyoxal bis[2-hydroxy-anil] may be a suitable indicator for the titration of calcium with EDTA. Further studies along this line are being made.

ACKNOWLEDGEMENTS

The authors are greatly indebted to Prof. Dr. FRITZ FEIGL for his valuable suggestions and constant interest in their work.

They also thank the Conselho Nacional de Pesquisas for financial support.

SUMMARY

It was found that glyoxal bis[2-hydroxy-anil] is a sensitive reagent for calcium. When the reaction is carried out as a spot test, as little as 0.05 μg Ca can be detected. If appropriate conditions are maintained, the calcium test is specific. The test described is specially suited to detect calcium oxide in a mixture of other colourless oxides, as well as to detect calcium in pharmaceutical preparations.

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Received March 24th, 1958

DETERMINATION OF ThO_2 IN THORIATED TUNGSTEN WIRE

by

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INTRODUCTION

The addition of thoria to tungsten filaments has been used for many years to increase the electron emission. The method of analysis of these filaments for thoria has been the one described by BROPHY AND VAN BRUNT[1].

This method involves the oxidation of the sample in a furnace at 700°–800° in a current of oxygen over night and the subsequent selective volatilization of the tungsten as the oxychloride. The latter step is attained by heating the oxidized sample at 800° in a stream of oxygen and hydrogen chloride (1:1) for 4–5 h. The residual ThO_2 is weighed and the volatilization step repeated until constant weight is obtained.

A procedure less time-consuming was desired. The many applications of EDTA for the determination of metals volumetrically[2] and particularly the application of EDTA for the titration of thorium[3] indicated that an improved method could be developed using EDTA.

Preliminary investigations with a standard solution of thorium showed that large amounts of tungsten interfere in the reaction between EDTA and thorium. It was found that an adequate separation could be attained by precipitation of the thorium several times as the hydroxide with sodium hydroxide.

PROCEDURE

Add 15 ml of hydrofluoric acid (48%) and 3 ml of concentrated nitric acid to a 1-g sample in a platinum dish. After the sample dissolves, 6 ml of 1 : 1 sulfuric acid are added and the solution taken to copious fumes of sulfuric acid. Cautiously wash the solution and precipitate into a 250-ml beaker and dilute to about 30 ml. Cautiously neutralize the mixture with 50% potassium hydroxide from a polyethylene wash bottle until the solution is strongly alkaline (pH 10–14 with wide range pH paper). Transfer the solution and precipitate to a 50-ml centrifuge tube. After centrifuging, discard the supernatant liquid (several steps are necessary to complete the transfer of the sample to the centrifuge tube) and add 4–5 ml of concentrated hydrochloric acid, 15–20 ml of water, and sufficient potassium hydroxide to make the solution alkaline. Dilute the solution to about 45 ml with water and centrifuge again. Decant the supernatant liquid and repeat the dissolution and precipitation of the thorium twice. Finally add 3–4 ml of concentrated hydrochloric acid to the precipitate remaining in the centrifuge tube and wash the resulting solution into a 250-ml beaker. Add a carefully measured quantity of 0.01 M EDTA solution in excess of that required to complex the Th estimated and 10 ml of acetate buffer (pH 4.7, 0.5 M each NaAc and HAc). Neutralize the solution with potassium hydroxide to a pH 4–5, add 4–5 drops of PAN and back titrate the excess of EDTA with a standard copper solution (0.01 M). Calculate per cent of ThO_2 from the following expression:

$$\%\,ThO_2 = \frac{(V_{EDTA} \cdot F - V_{Cu})\ (264.1)\ M_{Cu} \cdot 100}{\text{mg of sample}}$$

where V_{EDTA} and V_{Cu} represent the volumes of standard EDTA and copper solutions used and F is the volume (in ml) of standard copper solution whose molarity is M_{Cu} equivalent to one ml of the standard EDTA solution.

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DISCUSSION

After the neutralization of the sample solution, a considerable quantity of sulfate crystallizes out. This salt is transferred to the centrifuge tubes along with the thorium precipitate and is removed during the subsequent purification steps. A small amount of tungsten remains after the washing steps but does not interfere in the thorium titration.

Care should be taken to evaporate the sample solution to dense fumes of sulfuric acid. Failure to do so will result in an incomplete conversion of the thoria present in the sample to a soluble sulfate and low values will result.

Table I gives the results of some analyses with a standard solution to which sodium tungstate has been added in order to determine the effectiveness of the separation. Values are also given in Table I for a thoriated tungsten wire with and without an added amount of standard thorium solution.

TABLE I

Sample no.	*mg ThO_2 added*	*g Na_2WO_4 added*	*g Wire sample**	*mg ThO_2 found*
1	12.8	–	–	12.8
2	12.8	–	–	12.8
3	12.8	–	–	12.7
4	12.8	–	–	12.8
5	12.8	1	–	12.7
6	12.8	1	–	12.8
7	12.8	1	–	12.8
8	—	–	1	19.9
9	—	–	1	19.9
10	—	–	1	19.8
11	—	–	1	19.1
12	12.8	–	1	32.7
13	12.8	–	1	32.6
14	12.8	–	1	32.6
15	12.8	–	1	32.6

* Wire sample contains 2% ThO_2.

SUMMARY

Dissolution of a thoriated tungsten wire in a mixture of nitric and hydrofluoric acids followed by a sodium hydroxide separation of tungsten and EDTA titration of the thorium is used as an improved method for the determination of thorium in thoriated tungsten wire.

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Received March 3rd, 1958

EMPLOI DU „CADION" EN CHIMIE ANALYTIQUE

II. UN MICRODOSAGE SPECTROPHOTOMÉTRIQUE DU MERCURE

par

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INTRODUCTION

Le travail antérieur[1] consacré à l'utilisation du Cadion pour un dosage spectrophotométrique de l'ion cadmium, avait fait apparaître que l'ion mercurique se comporte vis-à-vis du réactif utilisé de la même façon que l'ion cadmium, ce qui oblige pour le dosage de ce dernier à une séparation préalable du mercure.

On envisage dans ce qui suit l'application du cadion au dosage spectrophotométrique de l'ion mercurique.

TECHNIQUE PROPOSÉE

La technique est tout à fait semblable à celle utilisée pour le cadmium, à quelques variantes près. Préparer les solutions suivantes:

a. *Solution-mère de cadion à 0.02%*. Peser 20 mg de cadion, dissoudre dans une solution alcoolique d'hydroxyde de potassium 0.02*N*, compléter à 100 ml avec le même solvant. Filtrer sur verre fritté No. 4 après 24 heures. Cette solution est d'une bonne conservation (garder le flacon bien bouché pour éviter l'action du CO_2 atmosphérique).

b. *Solution complexe*

Solution de cadion à 0.02%	10 ml
KOH aqueuse 2*N*	25 ml
Alcool à 95°	50 ml
Solution de tartrate de potassium et de sodium à 20%	5 ml
Solution de polyvinylpyrrolidone à 25%	1 ml
Eau redistillée dans le verre	q.s.p. 100 ml

Cette solution est préparée extemporanément pour chaque série de dosages.

c. *Solution-mère de mercure $10^{-3}M$* préparée à partir de chlorure mercurique pur pour analyses.

d. *Solution diluée de mercure*. Au moment de l'emploi, préparer une solution aqueuse 1 ml = 2 µg Hg par dilution de la solution-mère de mercure $10^{-3}M$.

MODE OPÉRATOIRE

Dans une fiole jaugée de 25 ml introduire 10 ml exactement mesurés de la solution complexe puis la prise d'essai d'ion mercurique à doser. Compléter au volume de 25 ml avec de l'eau redistillée. Établir dans les mêmes conditions une gamme-étalon de façon que le titre en Hg des solutions finales soit compris entre 0.05 et 1.4 p.p.m.

Le témoin est préparé en mesurant 10 ml de la solution complexe et en complétant au volume de 25 ml avec de l'eau redistillée.

Après 30 min à la température du laboratoire, déterminer à l'aide d'un photomètre la différence des densités optiques du témoin et de chaque essai pour la longueur d'onde de 560 mµ et sous une épaisseur de 1 cm.

La présence de mercure diminuant la densité optique, faire le zéro de l'appareil sur chaque essai, puis mesurer la densité optique du témoin.

La teneur en mercure de la prise d'essai est déduite de la courbe d'étalonnage établie.

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DISCUSSION ET PARTIE EXPÉRIMENTALE

Spectres d'absorption

Les densités optiques expérimentales du réactif avec et sans mercure ont été déterminées à l'aide du spectrophotomètre pour les longueurs d'onde de 400 à 600 mμ. Les résultats sont indiqués dans la Fig. 1. En présence d'un excès d'ion mercurique (5 p.p.m.) le maximum d'absorption se situe vers 460 mμ, l'écart maximum entre les deux courbes reste comme pour le cadmium à 560 mμ.

Cette dernière longueur d'onde a été utilisée pour les mesures, ici encore on mesure l'excès de colorant restant après formation de la laque.

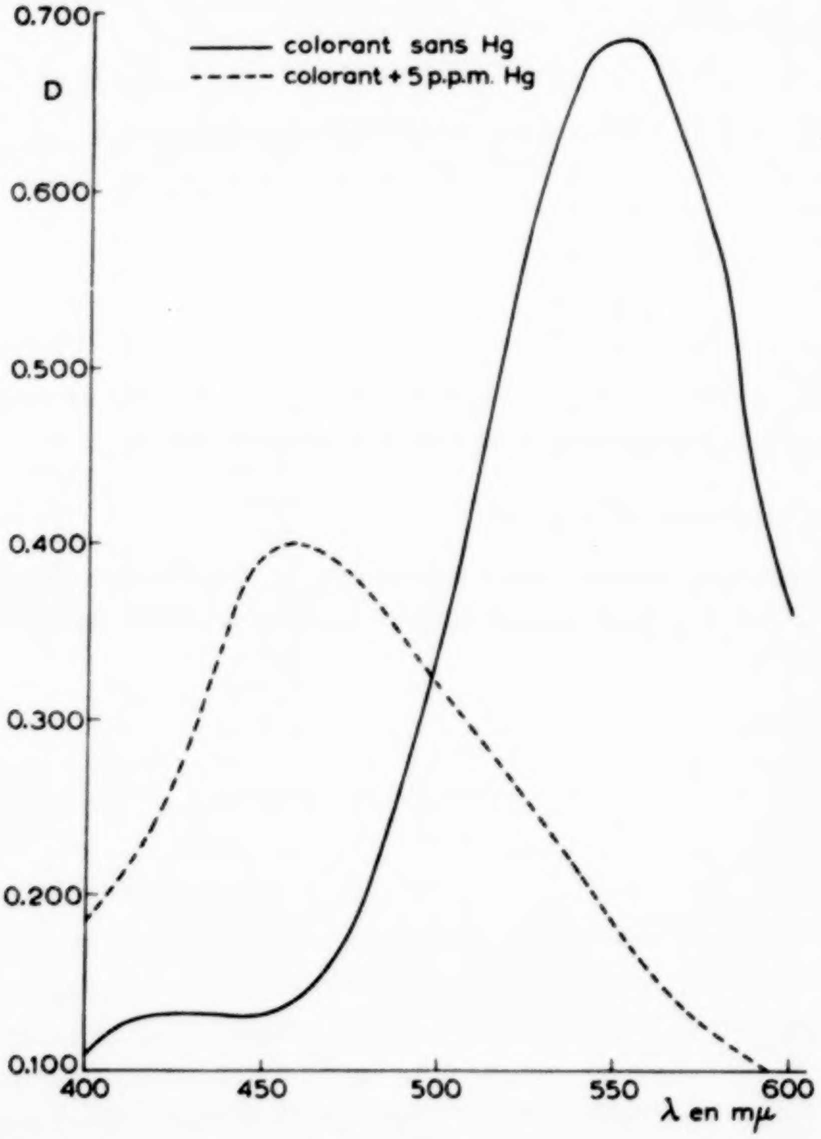

Fig. 1. Spectres d'absorption du réactif avec et sans mercure.

Influence du temps

Pour deux doses fixes d'ion mercurique, à la température de +20°, on a étudié l'évolution de la réaction dans le temps.

Nous voyons donc, que dans les conditions expérimentales utilisées, la réaction évolue lentement avec le temps, aussi doit-on lire les résultats après un temps déterminé (30 min par exemple).

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TABLEAU I

Hg dans la solution finale	*Densités optiques après:*						
	15 min	*30 min*	*45 min*	*60 min*	*80 min*	*105 min*	*120 min*
0.25 p.p.m.	0.172	0.164	0.158	0.155	0.153	0.150	0.147
0.75 p.p.m.	0.518	0.508	0.497	0.490	0.482	0.472	0.465

Influence de la température

Pour deux doses fixes d'ion mercurique on a laissé se développer la réaction pendant 30 min à des températures variables; les lectures ont été pratiquées immédiatement les 30 min écoulées.

TABLEAU II

Hg dans la solution finale	*Densités optiques après 30 min à*		
	+ 15°	+ 20°	+ 30°
0.2 p.p.m.	0.136	0.135	0.122
1 p.p.m.	0.660	0.675	0.640

Il sera préférable d'opérer à une température fixe, +20° par exemple.

Tous les essais ont été pratiqués à la lumière solaire diffuse.

Influence des doses variables de mercure

Pour une dose fixe de cadion nous avons étudié l'influence de doses d'ion mercurique variant de 0 à 2 p.p.m. Les résultats sont objectivés dans le Tableau III et la Fig. 2.

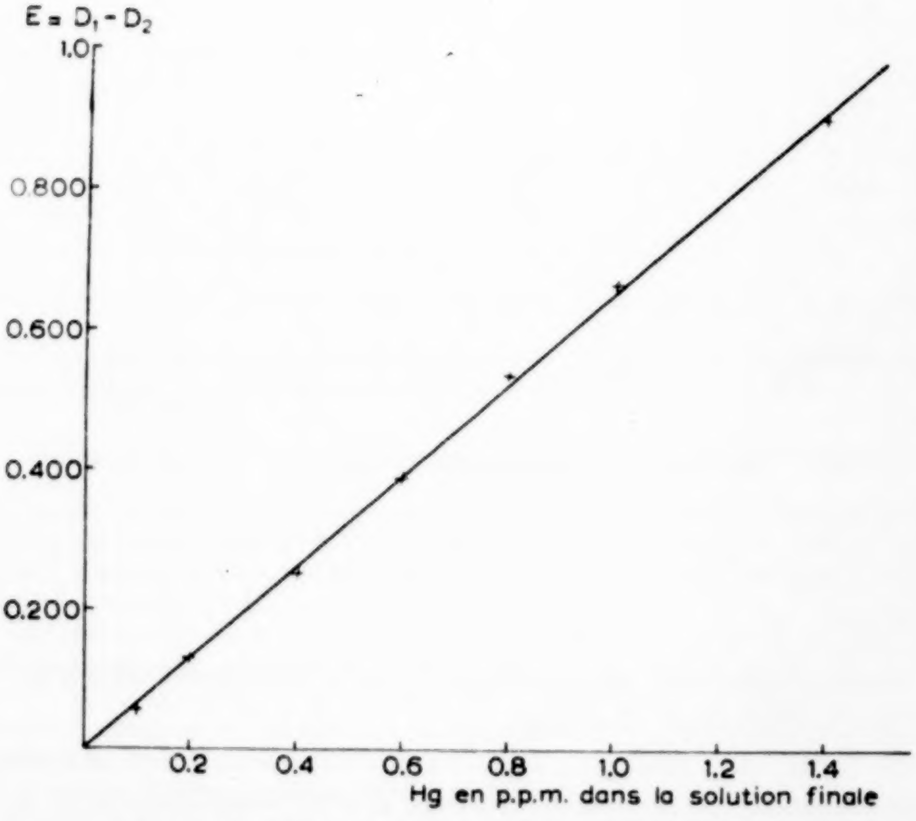

Fig. 2. Courbe d'étalonnage (spectrophotomètre).

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TABLEAU III

Hg dans la solution finale en p.p.m.	*0.1*	*0.2*	*0.4*	*0.6*	*0.8*	*1*	*1.2*	*1.4*	*2*
Densité optique lue (témoin—essai)	0.058	0.130	0.255	0.390	0.530	0.660	0.775	0.905	1.04

La loi de Beer est suivie de 0 à 1.4 p.p.m., au-delà la courbe s'infléchit.

Pratiquement il convient d'effectuer les dosages pour des teneurs entre 0.05 et 1.4 p.p.m. dans la solution finale.

Étude de la reproductibilité et de l'exactitude du dosage

Nous avons pratiqué 10 dosages pour une teneur de 1 p.p.m. en ion mercurique. Les résultats figurent dans le Tableau IV.

TABLEAU IV

No. des essais	*Densité optique*	*Hg ajouté en p.p.m.*	*Hg trouvé en p.p.m.*
1	0.660	1	1.01
2	0.655	1	1.00
3	0.660	1	1.01
4	0.650	1	0.99
5	0.650	1	0.99
6	0.645	1	0.985
7	0.650	1	0.99
8	0.640	1	0.98
9	0.645	1	0.985
10	0.650	1	0.99

Moyenne : 0.993 p.p.m.
Erreur quadratique moyenne : 0.012 p.p.m. soit 1.2%

Étude des ions étrangers

L'influence des ions les plus usuels sur le dosage de l'ion mercurique a été examinée.

L'étude a été pratiquée à l'aide du spectrophotomètre Jobin et Yvon sur 35 ions, dont 18 anions et 17 cations pour une quantité de 0.5 p.p.m. de mercure.

Les résultats sont reproduits dans les Tableaux V et VI.

Parmi les anions, CN^- inhibe complètement la réaction, ce qui n'a rien d'étonnant puisque la solidité du complexe de cyanure mercurique est bien connue.

Autre ion complexant du mercure, I^- interfère, mais à dose beaucoup plus forte.

AsO_2^- gène aussi la réaction par son pouvoir réducteur et complexant.

Parmi les cations, Sn^{+2} inhibe la réaction (réduction); Sb^{+3} à l'état d'émétique, gène également le dosage.

Tous les autres cations essayés (alcalins, alcalino-terreux, métaux lourds) ne perturbent pas la réaction, tout au moins aux doses essayées.

En comparant ces résultats à ceux obtenus dans l'étude des ions étrangers pour le dosage du cadmium, il semble que le cadion ait plus d'affinité pour le mercure que pour le cadmium.

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TABLEAU V

Nature de l'ion	*Sel utilisé*	*Rapport* $\frac{\text{ion étranger}}{\text{Hg}}$	*Hg ajouté en p.p.m.*	*Hg trouvé en p.p.m.*
F^-	NaF	1.000	0.5	0.50
Cl^-	KCl	1.000	0.5	0.49
Br^-	KBr	1.000	0.5	0.50
I^-	KI	100	0.5	0.50
		1.000	0.5	0.42
BO_2^-	$B(OH)_3$	1.000	0.5	0.50
CO_3^{-2}	K_2CO_3	1.000	0.5	0.50
$H_2PO_4^-$	KH_2PO_4	1.000	0.5	0.50
NO_3^-	KNO_3	1.000	0.5	0.50
NO_2^-	KNO_2	1.000	0.5	0.50
SO_4^{-2}	K_2SO_4	1.000	0.5	0.50
$HAsO_4^{-2}$	Na_2HAsO_4	100	0.5	0.50
		1.000	0.5	0.45
AsO_2^-	As_2O_3	10	0.5	0.44
		100	0.5	0.08
		1.000	0.5	0
ClO_3^-	$KClO_3$	1.000	0.5	0.50
CrO_4^{-2}	K_2CrO_4	1.000	0.5	0.50
CN^-	KCN	5	0.5	0
		1.000	0.5	0
CH_3COO^-	CH_3COONa	1.000	0.5	0.51
Oxalate	$(COOH)_2$	1.000	0.5	0.50
Citrate	NaCitrate	1.000	0.5	0.50

TABLEAU VI

Nature de l'ion	*Sel utilisé*	*Rapport* $\frac{\text{ion étranger}}{\text{Hg}}$	*Hg ajouté en p.p.m.*	*Hg trouvé en p.p.m.*
NH_4^+	NH_4Cl	1.000	0.50	0.51
Li^+	LiCl	100	0.50	0.50
Na^+	NaCl	1.000	0.50	0.50
Mg^{+2}	$MgCl_2$	10	0.50	0.50
		50	0.50	0.46
Ca^{+2}	$CaCl_2$	100	0.50	0.50
Mn^{+2}	$MnCl_2$	10	0.50	0.50
		50	0.50	0.41
Fe^{+3}	$FeCl_3$	10	0.50	0.49
		100	0.50	0.49
Co^{+2}	$CoCl_2$	10	0.50	0.46
		100	0.50	0.45
Ni^{+2}	$NiSO_4$	10	0.50	0.49
		100	0.50	0.53
Cu^{+2}	$Cu(NO_3)_2$	100	0.50	0.50
Zn^{+2}	$ZnSO_4$	100	0.50	0.50
Tl^+	Tl_2SO_4	100	0.50	0.50
Sn^{+2}	$SnCl_2$	5	0.50	0.50
		10	0.50	0.09
		100	0.50	0
Pb^{+2}	$Pb(CH_3COO)_2$	100	0.50	0.49
Sb^{+3}	Emétique	5	0.50	0.31
		10	0.50	0.20
		100	0.50	0
Bi^{+3}	$Bi(NO_3)_3$	100	0.50	0.50
Al^{+3}	$Al_2(SO_4)_3$	100	0.50	0.50

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RÉSUMÉ

Il est proposé un nouveau microdosage spectrophotométrique de l'ion mercurique, utilisant un colorant triazène, le ,,Cadion". La méthode est très sensible et précise si l'on respecte des conditions expérimentales bien déterminées. L'influence des ions étrangers a été indiquée.

SUMMARY

A new method is described for spectrophotometric microdetermination of the mercury ion by means of a triazine dye, the "Cadion". If the well-defined experimental conditions are maintained, the method is very sensitive and accurate. The influence of foreign ions is described.

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Reçu le 24 janvier 1958

STUDIES ON OXINE AND ITS DERIVATIVES

THE SENSITIVITY AND SELECTIVITY OF SOME 7-SUBSTITUTED 8-HYDROXYQUINOLINE-5-SULPHONIC ACIDS AND SOME 2-SUBSTITUTED 8-HYDROXYQUINOLINE-4-CARBOXYLIC ACIDS TOWARDS CERTAIN METALS*

by

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INTRODUCTION

Since the pioneer researches of BERG AND HAHN into the analytical applications of oxine and certain of its halogenated derivatives, search has continued for derivatives showing greater selectivity than the parent compound with regard to chelation with trace metals in solution. The fact that oxine itself chelated with a considerable number of metals[1] caused considerable difficulties in analytical practice, and indeed, it was only by removal of interfering metals or by 'masking' with other reagents, that oxine could be employed for the determination of a specific metal in the presence of others. Consequently a great number of techniques was published, employing oxine as the precipitating agent, in which interfering metals were complexed with other reagents or removed by physical methods, to give reliable methods for the determination of one metal in the presence of others.

Some years after BERG's initial researches, certain derivatives of oxine were employed in which substitution of halogen groups or solubilising groups (*e.g.* sulphonic acid groupings) conferred a certain degree of selectivity, but it is only comparatively recently that a greater understanding of the underlying theory involved has given a more complete picture of the phenomenon of selectivity.

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* Paper read at XVth International Congress of Pure and Applied Chemistry, (Analytical) Lisbon 1956. Section VI, Organic Complexes.

Through the years research has been directed along three main lines (*a*) the formation of heavier chelates by the introduction of halogen groupings in positions 5 or 7 of the quinoline ring (*e.g.* 5,7-dichloro-, 5,7 dibromo-, and 5,7-di-iodo-oxines), where a 'weighing effect' with the formation of complexes more stable in solutions of lower pH has conferred a certain degree of selectivity on the derivative; (*b*) the introduction of groupings in positions 2 and/or 7, giving derivatives in which the possibility of steric hindrance to chelate formation exists (*e.g.* 2-methyloxine, 7-methyloxine), and (*c*) the introduction of 'solubilising groups' such as sulphonic or carboxylic acid groupings, giving, in certain cases, water soluble chelates.

Although steric hindrance to chelation has been shown to play an important part in conferring selectivity, other factors have to be taken into account so that anomalous behaviour on the part of certain derivatives may be explained (see below). In the work now described some derivatives of oxine-5-sulphonic acid containing comparatively large groupings in position 7 have been prepared and examined. With these derivatives the possibility of steric hindrance to chelate formation, coupled with increased water solubility of the chelate exists. Both the above possibilities also exist in the other class of oxine derivatives prepared and examined, namely the 2-substituted oxine-4-carboxylic acids.

Although some derivatives of oxine-5-sulphonic acid containing small groupings *e.g.* halogens, nitroso, nitro in position 7 have been reported[2,3] and their reactions towards some metals examined, no derivatives containing comparatively large groupings in the sterically hindering position 7 have been investigated, and it seemed of interest to examine the behaviour of such derivatives towards some metallic ions.

With the other class of compounds, although some carboxylic acid derivatives containing carboxylic acid groupings in positions 4 or 5 have been reported[4,5] no derivatives containing a carboxylic acid grouping in position 4 and a substituent in position 2 have been critically examined with respect to their behaviour with a range of metal ions under standard conditions.

As substitution in position 2 is known to cause steric hindrance to chelate formation[6-8], and the effect of a carboxylic acid grouping will be to form water soluble chelates, the analytical potentialities of this class of oxine derivative seemed well worth investigating.

A great degree of selectivity is conferred by the introduction of sterically hindering groupings in positions 2 and 7 of the oxine ring and the selectivity is further enhanced by the increased water solubility of the chelates conferred by the presence of the sulphonic acid or carboxylic acid groupings. The increased selectivity is outweighed however by the concomitant decrease in sensitivity.

Of particular interest is the formation of a precipitate with aluminium and 8-hydroxy-2-*n*-hexylquinoline-4-carboxylic acid, this oxine derivative being unusual in precipitating aluminium from solution under the conditions of the test, although containing a substituent in position 2. Steric hindrance factors have prevented the formation of a aluminium *tris*-complex with many other 2-substituted oxine derivatives[6-8].

EXPERIMENTAL

Preparation of derivatives

7-Substituted 8-hydroxyquinoline-5-sulphonic acids. These were prepared by the reaction of the required base and formaldehyde with 8-hydroxyquinoline-5-sulphonic acid, working in ethanol solution.

8-Hydroxy-7-morpholinomethylquinoline-5-sulphonic acid. 8-Hydroxyquinoline-5-sulphonic acid (4 g recrystallised from 2 % hydrochloric acid) was stirred with 75 ml of anhydrous ethanol. To the slurry was added 4 ml of formaldehyde (35%) and 4 ml of morpholine. On the addition of the morpholine the 8-hydroxyquinoline-5-sulphonic acid remaining undissolved went into solution. The deep orange solution was boiled for 5 min when the required derivative began to precipitate. The mixture was allowed to stand for 3 h with water cooling, then filtered, rinsed with 25 ml of anhydrous ethanol and dried at 40°. Yield 6.1 g of off-white crystalline material. Melting point (recrystallised from anhydrous ethanol) 235° (uncorr.) Found C = 51.4%; H = 5.05%; N = 8.6%. $C_{14}H_{16}O_5N_2S$ requires C = 51.8%; H = 5.0%; N = 8.7%.

8-Hydroxy-7-piperidinomethylquinoline-5-sulphonic acid. This was similarly prepared from 8 g of 8-hydroxyquinoline-5-sulphonic acid, 8 ml of formaldehyde and 8 ml of piperidine. Yield 8.5 g. Melting point (after two recrystallisations from anhydrous ethanol) 238° (uncorr.).

Found C = 55.7%; H = 5.6%; N = 8.7%. $C_{15}H_{18}O_4N_2S$ requires C = 55.9%; H = 5.6%; N = 8.7%.

2-Substituted 8-hydroxyquinoline-4-carboxylic acids. These derivatives were prepared by refluxing *o*-aminophenol with pyruvic acid and the required aldehyde. The preparation of 8-hydroxy-2-(3,4-dimethoxyphenyl)-quinoline-4-carboxylic acid has previously been reported[9]. HOLDSWORTH AND LIONS[10] during an investigation into the preparation of analogues of cinchophen, described the preparation of 2-veratryl-7-hydroxyquinoline-4-carboxylic acid and 2-veratryl-6-hydroxyquinoline-4-carboxylic acid from *m*- and *p*-aminophenol respectively, but no preparations employing *o*-aminophenol were carried out.

It is know that other alternative methods of ring closure may operate in closely similar cases, but proof of the formation of 2-substituted 8-hydroxyquinoline-4-carboxylic acid derivatives by this reaction may be cited here. DOEBNER AND FETTBACK[11] have prepared 2-phenyl-oxine-4-carboxylic acid by refluxing *o*-aminophenol with benzaldehyde and pyruvic acid in ethanol solution. On decarboxylation 2-phenyl-oxine was obtained, identical with samples obtained by unambiguous synthesis (see IRVING *et al.*[12]). It was found that the required reaction proceeded most satisfactorily when freshly prepared *o*-aminophenol was employed. This was prepared as required by reduction of *o*-nitrophenol with sodium dithionite in alkaline solution following the method of PETROW AND STURGEON[13]. The *o*-aminophenol so prepared was kept moist with anhydrous ethanol until required.

8-Hydroxy-2-(3,4-dimethoxyphenyl)-quinoline-4-carboxylic acid. *o*-Aminophenol (14 g freshly prepared) was dissolved in 300 ml of ethanol and to the warm (50°) solution was added a mixture of 8.4 g of pyruvic acid and 14 g of veratraldehyde dissolved in 150 ml of anhydrous ethanol. The reactants were stirred and refluxed for 4 h. After standing overnight the required derivative had precipitated. This precipitate was removed, rinsed with anhydrous ethanol and dried at 40° to give 15 g of yellow powder. Melting point (recrystallised from anhydrous ethanol) 237° (uncorr.). Found C = 66.6%; H = 4.4%; N = 4.3%. $C_{18}H_{15}O_5N$ requires C = 66.4%; H = 4.6%; N = 4.3%.

8-Hydroxy-2-n-hexylquinoline-4-carboxylic acid. This was similarly prepared using 10 g of *o*-aminophenol, 6 g of pyruvic acid and 12.5 g of *n*-heptyl aldehyde. After refluxing, the initial volume of solution (130 ml) was reduced to 50 ml. On standing overnight the required precipitate was removed, rinsed with ethanol and dried *in vacuo* at 40°. Yield 7 g. It was necessary to recrystallise three times from anhydrous ethanol to obtain a pure material. Melting point 137–139° (uncorr). Found C = 69.9%; H = 7.1%; N = 5.1%. $C_{16}H_{19}O_3N$ requires C = 70.4%; H = 7.0%; N = 5.1%.

8-Hydroxy-2-(1-ethylpropyl)-quinoline-4-carboxylic acid. Similarly prepared from 20 g of *o*-aminophenol in 200 ml of anhydrous ethanol and 12 g of pyruvic acid and 22 g of 2-ethylbutyraldehyde in 50 ml of the same solvent. The volume was reduced to 100 ml after 4 h reflux. Yield 9 g. Melting point (after recrystallisation from anhydrous ethanol) 205° (uncorr.). Found C = 69.3%; H = 6.6%; N = 5.6%. $C_{15}H_{17}O_3N$ requires C = 69.5%; H = 6.6%; N = 5.4%.

Testing procedure for reagents with metals

Sensitivity tests. The theoretical basis for sensitivity tests has been discussed in detail by IRVING AND ROSSOTTI[14]. As these authors point out, a prediction of the behaviour of any new derivative from a consideration of the relevant physical properties and stability constants of its complexes with metals is not possible in practice, as insufficient data are available and the required equations are complicated by competitive complex formation. A more empirical approach is necessary, such an approach being the performance of sensitivity tests[12,15,16]. The method based on that suggested by LUTZ[15] modified by IRVING *et al.*[12], previously employed by HOLLINGSHEAD[16] is used here. This consists essentially in recording the sensitivity of the reagent in terms of the smallest amount of metal which will give a perceptible precipitate or colour change in a test solution under standard conditions. Three buffer solutions A, B and C having pH's of 5.3, 8.35 and 13.1 respectively are employed, and for each test the total volume of solution is kept constant at 7 ml. One outstanding disadvantage of the technique is that the composition and pH of the buffer solutions A, B and C are purely arbitrary. Precipitation reactions of some metal–reagent combinations may occur in a narrower pH range and may therefore be overlooked. This could be overcome by increasing the number of buffer solutions employed, but it is unlikely that information of great use would result from the considerable extra labour required.

It must also be born in mind that the appearance of a precipitate in one of the sensitivity tests under conditions of great dilution, while forming the basis of a spot-test reaction, must not be regarded as suitable for quantitative purposes, as precipitation may not be quantitative or the complex stoichiometric in its composition. The presence or absence of precipitates in a series of sensitivity tests with a new reagent may well give rise therefore to erroneous conclusions regarding its possibilities as a selective quantitative reagent. This is clearly illustrated in the investigation of 8-hydroxy-5-nitrosoquinoline previously reported[17].

Preparation of buffer, reagent and metal solutions and method of testing reagents. The preparations of buffer and metal solutions have previously been described[12,15,16]. Reagent solutions were $M/50$ in ethanol wherever possible. Some solutions were $M/50$ in 1 : 1 ethanol–water. The method of testing reagents has previously been described[16].

RESULTS

8-Hydroxyquinoline-5-sulphonic acid

Reactions of 8-hydroxyquinoline-5-sulphonic acid with various metals have previously been reported in the literature. The reason for including tests with this oxine derivative in this instance was to obtain a comparison under the same conditions with the unsubstituted sulphonic acid derivative and derivatives containing substituents in position 7 of the quinoline ring.

Owing to the sparing solubility of oxine-5-sulphonic acid in anhydrous ethanol a hot (65°) saturated solution was employed.

Oxine-5-sulphonic acid precipitates copper, zinc, cobalt and cadmium from solutions of pH 5.3 *under the conditions of the test*. ALBERT AND MAGRATH[18] have carried out sensitivity tests (using a similar method to the one employed here previously reported by ALBERT AND GLEDHILL[19]).

At pH 7.0 no precipitation was observed by these workers with calcium, magnesium, manganese, zinc, ferrous and ferric iron, cadmium, cobalt, lead and copper, using a $0.005M$ reagent solution and a $0.0005M$ metal solution. ALBERT AND MAGRATH's findings regarding non-precipitation with the above metals from an approximately neutral solution are confirmed, no precipitation being observed in the present tests using a buffer of pH 8.35.

BERG[4] also reported that, apart from a slight tendency for copper and ferric ions to form precipitates from acid solutions, no method which might appear suitable for analytical purposes could be found for any metal. This statement appeared to refer to gravimetric or volumetric procedures only; colorimetric methods were not considered. BERG also noted that precipitation was prevented in neutral solutions containing tartrate ions. This has been confirmed.

Zinc is precipitated from acid solutions containing acetic acid and sodium acetate at pH 5.3. Previous reports of precipitation of the zinc complex appear conflicting. An early paper by VAISMAN[20] reported precipitation of the zinc complex using 8-hydroxyquinoline-7-sulphonic acid. MOLLAND[2] repeated this work and stated that the compound referred to as 8-hydroxyquinoline-7-sulphonic acid was undoubtedly 8-hydroxyquinoline-5-sulphonic acid. VAISMAN's method consisted in treating a solution of the zinc salt buffered with sodium hydroxide and sodium tartrate with an aqueous solution of the 'potassium salt of 8-hydroxyquinoline-7-sulphonic acid'. As the pH of this mixture would be alkaline, this method has not been confirmed in the present investigation where no precipitation was obtained with Buffer C containing sodium hydroxide and sodium potassium tartrate.

LIU AND BAILAR[21] have described the preparation of the zinc complex by precipitation from a solution containing zinc sulphate, sodium tartrate and sodium hydroxide, when on the addition of a solution of 8-hydroxyquinoline-5-sulphonic acid dissolved in potassium hydroxide solution followed by acetic acid until the pH is just acid, the zinc complex was obtained. Some doubt must be cast on VAISMAN's reported precipitation from alkaline solution.

The introduction of the hydrophilic acid grouping confers on the complexes a great degree of intrinsic solubility in water. The definite colour changes seen with Ni, Ga, In, Tl, and Y in acid and neutral solutions point to the formation of water soluble chelates (see Table II). Those metallic complexes which do precipitate only do so in acid solution; in neutral and alkaline solutions they remain in solution. The sensitivity of a precipitation reaction depends both on the stability of the metal complex and on its intrinsic solubility. From the stability constants of some divalent metals including Cd, Co, Zn, and Cu, given by NÄSÄNEN AND UUSITALO[22], however, it appears that the effect of the sulphonic acid grouping on the chelate stability is relatively slight, so that the decrease in sensitivity observed with 8-hydroxyquinoline-5-sulphonic acid would appear to stem from the increased water solubility of the chelates.

In Buffer C, with the highest concentration (4 ml of $M/100$) of certain metals, the solution remained clear after digestion, although precipitation of reagent, and in some cases, metal, occurred at this pH. This occurred with copper, nickel and cobalt, and denoted the formation of water soluble chelates under these conditions.

8-Hydroxy-7-morpholinomethylquinoline-5-sulphonic acid

A $M/50$ solution of the reagent was prepared in 1:1 ethanol–redistilled water, owing to the very sparing solubility of this derivative in absolute ethanol. After digestion at 50°, solution was complete and precipitation of the derivative did not occur on cooling.

With this derivative the possibility of steric hindrance to chelate formation exists, with the presence of the large morpholinomethyl grouping in position 7, in close proximity to the chelating function. This would possibly lead to a slight increase in selectivity, although the degree of steric hindrance obtained by substitution in position 7 does not appear to be as great as that conferred by a substituent in position 2. Outweighing any increase in selectivity due to the sterically hindering substituent in position 7, is the water solubility of the chelates conferred by the sulphonic acid grouping, leading to decreased sensitivity.

The results obtained with the metals examined show that, with the exception of copper, none of the metals give a precipitate, although colour changes, pointing to chelate formation occur with Ni, Al, Ga, In, Tl, Y, Zn, Mg, Cd, Co, and Fe^{+3}. The colour changes are generally of low sensitivity as would be expected (see Table II).

8-Hydroxy-7-piperidinomethylquinoline-5-sulphonic acid

This reagent precipitates in Buffer C, but not in Buffers A and B, where clear yellow solutions are obtained. The same conditions regarding steric hindrance to chelate formation being outweighed by increased water solubility of the chelates occurs with this derivative, and, with the exception of copper, none of the other metals tested gave insoluble chelates under the conditions of the test. Colour changes occurred with Ni, Al, Ga, In, Tl, Y, Zn, Mg, Cd, Co, and Fe^{+3}, but these were generally of low sensitivity (see Table II).

The formation of a water soluble chelate with cobalt in Buffer C is denoted by the non-precipitation of the reagent with the greatest concentration of the metal employed, although the reagent itself precipitates at this pH.

8-Hydroxy-2-(3,4-dimethoxyphenyl)-quinoline-4-carboxylic acid

As this compound is sparingly soluble in cold ethanol, a hot (50°) solution was used. With this derivative, the possibility of steric hindrance to chelate formation exists, coupled with enhanced water solubility of any chelate formed, due to the presence of the hydrophilic carboxylic acid grouping in position 4. This should lead to greatly increased selectivity coupled with decreased sensitivity. Precipitation did not occur with any of the metals examined. Colour changes were noted with Ni, Zn, Mg, Ga, In, Tl, Co, and Fe^{+3} (see Table II), denoting the formation of soluble chelates. No differences in colour were obtained in the Al, Y, and Cd tests, and it would appear that a small degree of selectivity is conferred by the presence of the comparatively large grouping in position 2.

The non-formation of a chelate with aluminium under these conditions confirms the previously reported behaviour of 2-substituted derivatives towards this metal, no precipitation occurring with many 2-substituted derivatives[6–8]. Chelation does not appear to take place with yttrium and cadmium. With this derivative the colour changes are of low sensitivity (see Table II). Although both the metal and the reagent precipitate individually in Buffer C, no precipitation occurs with 4 ml of *M*/100 cobalt, pointing to the formation of a soluble chelate or a mixed complex.

TABLE I

8-HYDROXY-2-*n*-HEXYLQUINOLINE-4-CARBOXYLIC ACID: SENSITIVITY TESTS

Metal	*M*	*Buffer*	*Tube examined*	V_1 *to* V_2[a]	*pL*[b]	*Colour*[c]
Cu^{+2}	0.01	A	H[d]	0.1–0.04	3.8–4.2	dark brown
Cu	0.001	A	C[e]	0.4–0.3	4.2–4.4	dark brown
Cu	0.01	B	H	0.1–0.04	3.8–4.2	yellow brown
Cu	0.001	B	C	0.3–0.2	4.4–4.5	brown
Cu	0.01	C	H+C	0.1–0.04	3.8–4.2	orange yellow
Ni^{+2}	0.001	A	H+C	0.4–0.3	4.2–4.4	yellow
Ni	0.001	B	H+C	0.4–0.3	4.2–4.4	brown yellow
Ni	0.01	C	H+C	NP[f]	–	
Al^{+3}	0.001	A	H+C	0.4–0.3	4.2–4.4	yellow

TABLE I (continued)

Metal	*M*	*Buffer*	*Tube examined*	*V_1 to V_2*[a]	*pL*[b]	*Colours*[c]
Al	0.01	B	H+C	NP	–	
Al	0.01	C	H+C	NP	–	
Ga^{+3}	0.01	A	H	0.2–0.1	3.5–3.8	yellow
Ga	0.001	A	C	0.4–0.3	4.2–4.4	yellow
Ga	0.01	B	H+C	0.2–0.1	3.5–3.8	yellow brown
Ga	0.01	C	H+C	NP	–	
In^{+3}	0.01	A	H+C	0.2–0.1	3.5–3.8	yellow
In	0.01	B	H+C	0.2–0.1	3.5–3.8	yellow
In	0.01	C	H+C	NP	–	
Tl^{+3}	0.001	A	H+C	0.4–0.3	4.2–4.4	yellow (rose pink) [g]
Tl	0.001	B	H+C	0.4–0.3	4.2–4.4	yellow (rose pink) [g]
Tl	0.01	C	H+C	NP	–	
Y^{+3}	0.01	A	H+C	4.0–3.0	2.2–2.4	yellow
Y	0.01	B	H+C	NP	–	
Y	0.01	C	H+C	NP	–	
Zn^{+2}	0.01	A	H+C	0.2–0.1	3.5–3.8	yellow
Zn	0.01	B	H+C	0.2–0.1	3.5–3.8	yellow
Zn	0.01	C	H+C	NP	–	
Mg^{+2}	0.01	A	H+C	NP	–	
Mg	0.01	B	H+C	4.0–3.0	2.2–2.4	brown
Mg	0.01	C	H+C	NP	–	(yellow)
Cd^{+2}	0.01	A	H+C	4.0–3.0	2.2–2.4	yellow
Cd	0.01	B	H+C	4.0–3.0	2.2–2.4	yellow
Cd	0.01	C	H+C	NP	–	
Co^{+2}	0.001	A	H+C	0.4–0.3	4.2–4.4	brown
Co	0.0001	B	H+C	0.3–0.2	5.4–5.5	orange brown
Co	0.01	C	H+C	NP	–	
Fe^{+3}	0.01	A	H+C	0.2–0.1	3.5–3.8	brown or green [h]
Fe	0.01	B	H+C	NP	–	(brown or green) [i]
Fe	0.01	C	H+C	NP	–	

[a] V_1 and V_2 are the volumes of standard metal solution which (1) give a precipitate or colour change and (2) fail to give a precipitate or colour change respectively.

[b] pL is defined as —log (limiting concentration), in g.equiv./l for the volumes V_1 and V_2 respectively[12]. This value is to be preferred as an expression of sensitivity as the use of μg/ml may convey a false impression of the difference in sensitivities of the reagent with metals of differing atomic weight or valency.

[c] Colours in parentheses refer to solutions and colours not in parentheses refer to colours of precipitates.

[d] Hot.

[e] Cold.

[f] NP = No precipitate.

[g] Before digesting at 70° a rose pink colouration occurs on the addition of reagent solution. This is destroyed on heating with the formation of a yellow precipitate.

Brown precipitate in tube containing the higher concentration of Fe^{+3}; green precipitate in tubes containing the lower concentrations.

Brown colouration in tube containing the higher concentration of Fe^{+3}; green colouration in tubes containing the lower concentrations.

8-Hydroxy-2-n-hexylquinoline-4-carboxylic acid

8-Hydroxy-2-*n*-hexylquinoline-4-carboxylic acid is readily soluble in absolute ethanol giving a yellow solution. From the results given in Table I it is seen that precipitation of all the metals examined occurs, although the sensitivity with magnesium, yttrium and cadmium is very low. The presence of the long aliphatic chain in position 2 of the quinoline ring does not confer a great degree of selectivity due to steric hindrance reasons, and in behaviour, this derivatives may be compared to oxine itself. Although the presence of the carboxylic acid grouping in position 4 would lead to the formation of water soluble complexes, so conferring enhanced selectivity, this appears to have been outweighed to a great extent by the aliphatic chain in position 2, which has caused large differences in the intrinsic solubilities of the chelates, with the formation of chelates which are less soluble in water than those of other 4-carboxylic acid derivatives examined. The overall sensitivity of this derivative approaches closely that of oxine itself, the pL values of the chelates being of the same order as those of the corresponding oxine chelates.

The most interesting behaviour of this derivative is its formation of a precipitate with aluminium at pH 5.3. Previous reports of non-chelation with this metal and other 2-substituted oxine derivatives have suggested steric hindrance factors to be responsible[6-8]. IRVING, BUTLER AND RING[12] confirmed MERRITT AND WALKER'S original observation[6], regarding non-chelation of 2-methyl-oxine with aluminium, and PHILLIPS *et al.*[7,8] demonstrated that other 2-substituted oxine derivatives did not give chelates with this metal. It is not clear why 8-hydroxy-2-*n*-hexylquinoline-4-carboxylic acid gives a precipitate under the conditions of the test. The nature of the precipitate is under investigation. With a branched chain aliphatic grouping in position 2 (see below) no precipitation occurs with aluminium under the same conditions.

PHILLIPS AND BARRALL[23] have reported that 7-(α-anilinobenzyl)-2-methyloxine and 7-[α-(*o*-carbethoxyanilino)-benzyl]-2-methyloxine both gave fluorescent yellow precipitates with aluminium in neutral solution. The authors further reported the fact that the spectrum of the aluminium compound of the latter derivative was almost identical with the spectrum of the reagent itself, rather than shifted to much longer wavelength as is usual with the chelate compounds of oxine, suggesting the possibility that the structure was either a salt or a relatively unstable chelate.

A further interesting observation with this derivative is the formation of a rose-pink colouration with trivalent thallium on the addition of the reagent. In Buffers A and B this rose-pink colouration presists for periods of up to 15 min without appreciable change. On digestion at 70° the colour is destroyed with the formation of a yellow precipitate. No pink colouration was obtained with any of the other Group IIIb metals under the same conditions, and this property may well form the basis of a spot test for the detection of trivalent thallium in the presence of all or any of the other metals of the sub-group. The colour change has the disadvantage of being transient and of medium sensitivity.

8-Hydroxy-*n*-hexylquinoline-4-carboxylic acid shows its greatest sensitivity towards cobalt in buffer B, where the limit of detection lies between 0.3 and 0.2 ml of 0.0001 *M* cobalt solution. The pL value is 1.4 units greater than that for cobalt oxinate.

TABLE II

LIMITING CONCENTRATIONS OF METALS GIVING COLOUR CHANGES WITH OXINE DERIVATIVES

Metal	*M*	*Buffer in which greatest sensitivity is shown*	*$V_1 - V_2$ ml*	*pL*	*Colour*
8-Hydroxyquinoline-5-sulphonic acid					
Cu^{+2}	0.01	B	0.4–0.04	3.2–4.2	emerald green
Ni^{+2}	0.001	B	0.4–0.3	4.2–4.4	apple green
Al^{+3}		A, B, C	NC [a]		
Ga^{+3}	0.01	A, B	0.4–0.04	3.2–4.2	green
In^{+3}	0.01	A, B	0.4–0.04	3.2–4.2	pale yellow
Tl^{+3}	0.01	A, B	0.1–0.04	3.8–4.2	yellow
Y^{+3}	0.01	A	0.4–0.3	3.2–3.4	pale yellow
Zn^{+2}	0.01	B	0.1–0.04	3.8–4.2	yellow
Mg^{+2}		A, B, C	NC		
Cd^{+2}	0.01	C	0.1–0.04	3.8–4.2	yellow
Co^{+2}	0.01	B	0.1–0.04	3.8–4.2	yellow brown
Fe^{+3}	0.001	A, B	0.3–0.2	4.4–4.5	emerald green
8-Hydroxy-7-morpholinomethylquinoline-5-sulphonic acid					
Ni^{+2}	0.01	B	0.2–0.1	3.5–3.8	apple green
Ga^{+3}	0.01	B	0.4–0.3	3.2–3.4	green yellow
In^{+3}	0.01	A, B	0.4–0.3	3.2–3.4	pale green
Tl^{+3}	0.01	A, B	0.4–0.3	3.2–3.4	pale green
Y^{+3}	0.01	A	0.4–0.3	3.2–3.4	pale yellow
Zn^{+2}	0.01	A, B	0.1–0.04	3.8–4.2	yellow green
Mg^{+2}	0.01	C	0.4–0.3	3.2–3.4	green yellow
Cd^{+2}	0.01	A	0.4–0.3	3.2–3.4	pale yellow
Co^{+2}	0.01	B	0.1–0.04	3.8–4.2	deep orange
Fe^{+3}	0.001	A, B	0.4–0.3	4.2–4.4	emerald green
8-Hydroxy-7-piperidinomethylquinoline-5-sulphonic acid					
Ni^{+2}	0.01	A, B	0.1–0.04	3.8–4.2	green
Al^{+3}	0.01	A, B	0.1–0.04	3.8–4.2	yellow
Ga^{+3}	0.01	A, B	0.1–0.04	3.8–4.2	pale green
In^{+3}	0.01	B	0.3–0.2	3.4–3.5	pale green
Tl^{+3}	0.01	A	0.4–0.3	3.2–3.4	green
Y^{+3}	0.01	A	0.4–0.3	3.2–3.4	pale green
Zn^{+2}	0.01	A, B	0.4–0.3	3.2–3.4	pale green
Mg^{+2}	0.01	B	0.4–0.3	3.2–3.4	pale green
Cd^{+2}	0.01	A	0.4–0.3	3.2–3.4	green yellow
Co^{+2}	0.01	A	0.4–0.3	3.2–3.4	yellow
Fe^{+3}	0.001	A, B	0.3–0.2	4.4–4.5	emerald green
8-Hydroxy-2-(3,4-dimethoxyphenyl)-quinoline-4-carboxylic acid					
Cu^{+2}	0.001	B	0.3–0.2	4.4–4.5	brown
Ni^{+2}	0.01	B	0.1–0.04	3.8–4.2	yellow
Al^{+3}		A, B, C	NC		
Ga^{+3}	0.01	A	0.2–0.1	3.5–3.8	orange
In^{+3}	0.01	B	0.1–0.04	3.8–4.2	orange yellow
Tl^{+3}	0.001	A, B	0.4–0.3	4.2–4.4	orange

TABLE II (continued)

Metal	*M*	*Buffer in which greatest sensitivity is shown*	$V_1 - V_2$ *ml*	*pL*	*Colour*
Y^{+3}		A, B, C	NC		
Zn^{+2}	0.01	B	0.2–0.1	3.5–3.8	yellow
Mg^{+2}	0.01	C	0.4–0.3	3.2–3.4	olive green
Cd^{+2}		A, B, C	NC		
Co^{+2}	0.01	A, B	0.2–0.1	3.5–3.8	orange yellow
Fe^{+3}	0.001	A, B	0.3–0.2	4.4–4.5	brown; orange yellow
8-Hydroxy-2-(1-ethylpropyl)-quinoline-4-carboxylic acid					
Cu^{+2}	0.01	A, B	0.2–0.1	3.5–3.8	olive green; green brown
Ni^{+2}	0.01	B	0.3–0.2	3.4–3.5	yellow
Al^{+3}		A, B, C	NC		
Ga^{+3}		A, B, C	NC		
In^{+3}	0.001	B	0.4–0.3	4.2–4.4	yellow
Tl^{+3}	0.001	A	0.4–0.3	4.2–4.4	yellow
Y^{+3}		A, B, C	NC		
Zn^{+2}	0.01	B	0.3–0.2	3.4–3.5	yellow
Mg^{+2}		A, B, C	NC		
Cd^{+2}	0.01	B	0.3–0.2	3.4–3.5	yellow
Co^{+2}	0.01	B	0.3–0.2	3.4–3.5	yellow
Fe^{+3}	0.001	B	0.2–0.1	4.5–4.8	emerald green

[a] NC = No discernable colour change.

8-Hydroxy-2-(1-ethylpropyl)-quinoline-4-carboxylic acid

This derivative is freely soluble in absolute ethanol, giving a yellow solution. With all the metals investigated, precipitation of a complex does not occur. Colour changes denoting chelate formation are found with Cu, Ni, Zn, In, Tl, Cd, Co and Fe^{+3} (see Table II). The carboxylic acid grouping, conferring water solubility on the chelates, appears to outweigh any influence the branched chain aliphatic grouping may have on the intrinsic solubility, so that water soluble chelates are formed under the conditions of the test. All these colour reactions are of low sensitivity (see Table II).

DISCUSSION

None of the derivatives investigated shows any striking analytical advantage over the parent compound. A large increase in water solubility of all the chelates was to be expected, due to the presence of sulphonic acid or carboxylic acid groupings, but the hope that sensitive colour changes, due to the formation of water-soluble chelates would form the basis of new spot test techniques has not been fulfilled. Such colour reactions as were observed have been, largely, of low sensitivity, precluding their analytical use. The one exception is the formation of a rose-pink colouration with trivalent thallium and 8-hydroxy-2-*n*-hexylquinoline-4-carboxylic acid. This may well form the basis of a spot test for the detection of this metal in the presence of others of the same sub-group.

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The hope that the weighing effect of the comparatively large groupings in position 7 of oxine-5-sulphonic acid would further enhance any degree of selectivity conferred by the presence of the solubilising sulphonic acid groupings has not been realised.

ACKNOWLEDGEMENTS

My thanks are due to the Directors of The British Drug Houses Ltd., for permission to publish this work.

SUMMARY

A number of new derivatives of 8-hydroxyquinoline containing both solubilising groups and groups which might sterically hinder chelation have been prepared, *viz.* 8-hydroxy-7-morpholinomethylquinoline-5-sulphonic acid, 8-hydroxy-7-piperidinomethylquinoline-5-sulphonic acid, 8-hydroxy-2-(3,4-dimethoxyphenyl)-quinoline-4-carboxylic acid, 8-hydroxy-2-*n*-hexylquinoline-4-carboxylic acid and 8-hydroxy-2-(1-ethylpropyl)-quinoline-4-carboxylic acid. The limiting sensitivities of the reactions of these reagents towards copper, nickel, aluminium, zinc, magnesium, gallium, indium, thallium, yttrium, cadmium, cobalt and iron have been investigated.

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Received March 1st, 1958

THE THORIUM-APANS COMPLEX

A SPECTROPHOTOMETRIC STUDY

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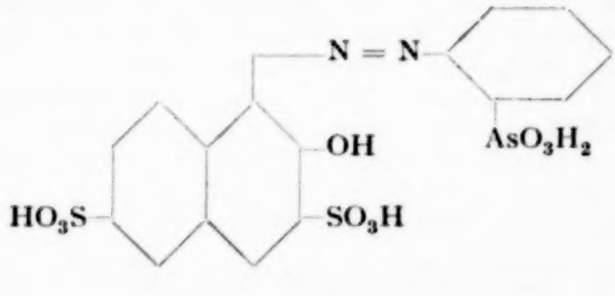
The reagent 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulphonic acid was first introduced by KUZNETSOV[1,2] in 1941 for the detection of thorium. THOMASON, PERRY AND BYERLY[3] used this reagent to develop a method for the determination of microgram quantities of thorium. Recently, FOREMAN, RILEY AND SMITH[4] have used the reagent to estimate microgram amounts of quadrivalent uranium.

The reagent is known by various trivial names: Thoron, thorin, thoronol, naphtharson and Apans. All names refer to the same material whose structural formula may be written:



The reagent is available commercially in the form of its disodium salt. In this communication, the trivial name Apans will be used for the reagent.

EXPERIMENTAL

Reagents

(*i*) *Apans solution.* 0.2611 g of the disodium salt (as supplied by B.D.H.) was dissolved in water and diluted to 1 l. This gave a solution $4.53 \cdot 10^{-4} M$.

(*ii*) *Thorium solution.* A solution prepared by dissolving A.R. thorium nitrate in water was standardised by precipitating the thorium as the hydroxide and igniting to constant weight. The solution thus prepared was $4.53 \cdot 10^{-2} M$. A solution $4.53 \cdot 10^{-4} M$ was prepared by dilution.

Absorption measurements were made with a Hilger "Uvispek" Spectrophotometer using 1-cm or 4-cm matched glass cells. The light source was a tungsten lamp.

The thorium–Apans complex

The structure of the thorium–Apans complex has been studied previously by BYRD AND BANKS[5] and CLINCH[6]. BYRD AND BANKS find that the complex is predominantly 2 moles of thorium to 3 moles of Apans. They state, however, that the results are inconclusive; although titration experiments also suggest a formula Th_2R_3.

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CLINCH[6] states that spectrophotometric analyses indicate that the complex is formed from one atom of thorium and two molecules of Apans. In view of this discrepancy, it was decided to reinvestigate this system.

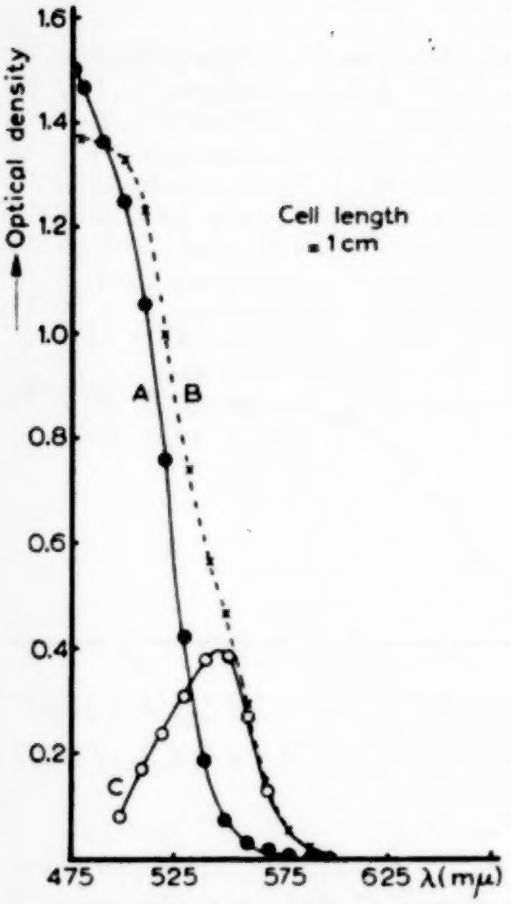

Fig. 1. Absorption spectra. A. Reagent *vs.* water. B. Complex *vs.* water. C. Complex *vs.* reagent.

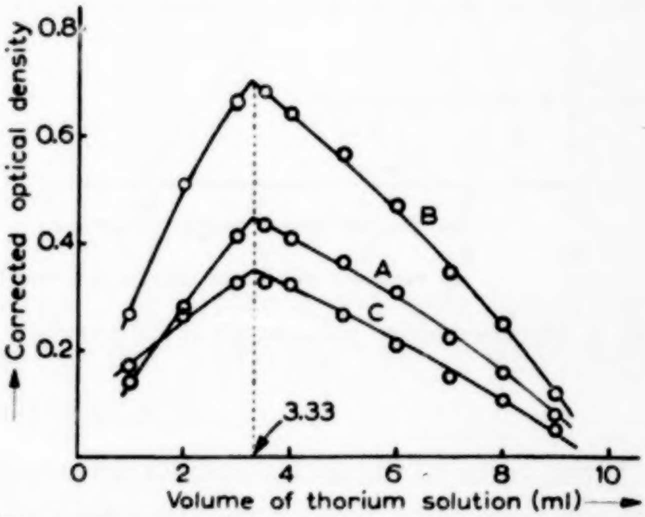

Fig. 2. JOB's method. A = 500 mμ, B = 530 mμ, C = 560 mμ.

Fig. 1 shows the spectra of the Apans reagent and the thorium–Apans complex. The addition of the reagent causes a shift to longer wavelengths. If the density of the complex is measured using a reagent solution as reference, a curve showing maximum density at 545 mμ is obtained.

The empirical formula of the thorium–Apans complex was investigated by the method of continuous variations[7–9] and by the slope ratio method[10,11]. For the continuous variations method, equimolar solutions ($4.53 \cdot 10^{-4} M$) of thorium and Apans were mixed in the proportions of x to $(10-x)$ ml, and made up to 100 ml. The pH of the final solution was adjusted to approximately 1 by the addition of appropriate quantities of nitric acid. Typical plots of corrected optical density against the parameter x are shown in Fig. 2.

It is evident that the complex contains 2 molecules of Apans to one of thorium. The correspondance of the curves at different wavelengths suggests the formation of only one complex. For the uranium^{IV}–Apans complex, FOREMAN *et al.*[4] find that the complex contains two molecules of Apans to one of uranium^{IV}.

The formula ThR_2 is also suggested by the evidence obtained by the slope ratio method. In this method, the optical densities *versus* the concentration of the variable

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component are plotted from two origins at either end of the X axis. Typical plots are shown in Fig. 3.

The molar optical density of the complex may be measured by preparing solutions containing an excess of reagent corresponding to the plateau in Fig. 4[12].

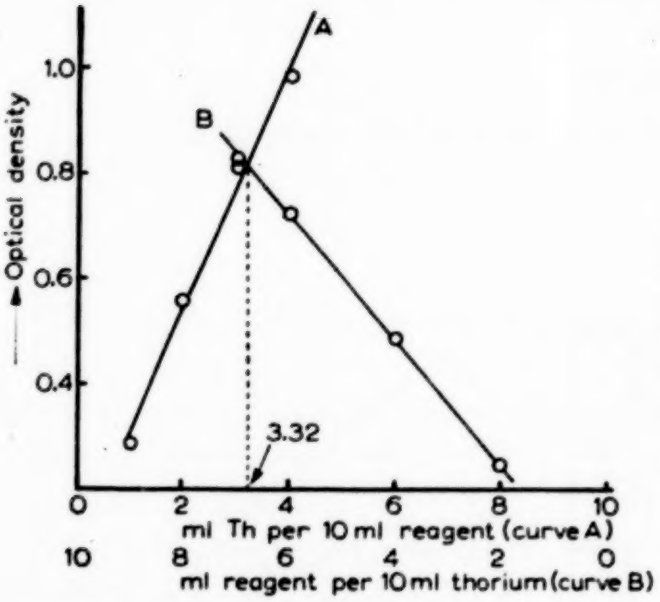

Fig. 3. Modified slope ratio method (at 530 mμ).

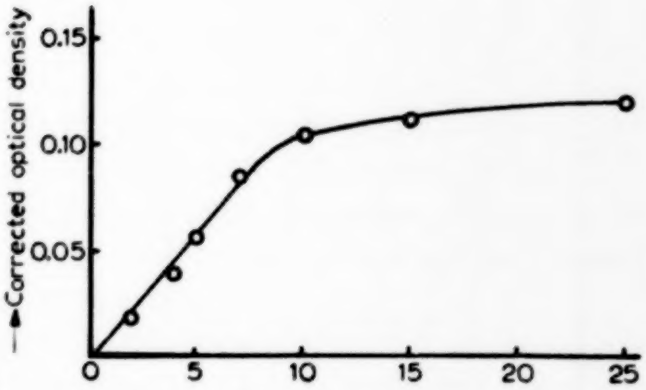

Fig. 4.

If the value of the molar optical density of the pure reagent is known; then provided the solutions obey Beers Law, the apparent stability constant K of the complex may be calculated[12] assuming that the formation is in accordance with the following equation

$$\mathrm{Th} + 2\mathrm{R} \rightleftarrows \mathrm{ThR_2}$$

where R represents the molecule of Apans

$$\text{Hence } K = \frac{[\mathrm{ThR_2}]}{[\mathrm{Th}]\cdot[\mathrm{R}]^2}$$

Application of this method to several solutions gave a value of $K = 1.4 \pm 0.1 \cdot 10^{10}$.

DISCUSSION

In the absence of information as to its charge, it is not possible to assign a structure to the complex. The sharp peak of the curves in JOB's procedure and the modified molar ratio method substantiate the high value of the stability constant.

No evidence was obtained for the stepwise formation of the complex, JOB's method giving similar results at the three wavelengths employed. The high value for the stability constant of the complex is further supported by dilution experiments. Varying amounts of thorium solution were mixed with equal amounts of Apans of the same molarity and diluted always to the same volume. In this way the concentration of the complex was varied ten fold in a series of experiments. Plots of optical density *versus* volume were linear.

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SUMMARY

The compound formed from thorium and Apans has been studied by spectrophotometric methods and shown to contain thorium and reagent in the ratio 1:2. The apparent stability constant of this complex has been measured as $1.4 \pm 0.1 \cdot 10^{10}$.

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Received March 6th, 1958

VOLUMETRIC DETERMINATION OF CALCIUM AND MAGNESIUM WITH ETHYLENEDIAMINETETRAACETIC ACID IN THE PRESENCE OF PHOSPHATE

by

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INTRODUCTION

Although the titration of calcium and magnesium with ethylenediaminetetraacetic acid (EDTA) is well known, little is mentioned in the literature regarding this titration in the presence of phosphate. Without enumerating all the references, mention must be made of some of the methods described.

BRUNISHOLZ, GENTON AND PLATTNER[1] eliminate phosphate with the aid of an ion-exchanger and determine calcium in the effluent. COLLIER[2] suggests the removal of phosphate prior to the EDTA titration of calcium and magnesium, by extraction with *n*-butanol in hydrochloric acid medium. CAMPEN AND NIJST[3] separate phosphate as iron phosphate; the excess of iron is precipitated with ammonia, and calcium and magnesium are then determined in the filtrate. KÁLMÁN AND VÁGÓ[4] remove phosphate by precipitation as ammonium phosphomolybdate prior to the determination of calcium and magnesium. KINNUNEN AND WENNERSTRAND[5] eliminate phosphate with beryllium, whereby the excess of beryllium is brought down with the precipitated beryllium phosphate as beryllium hydroxide. Calcium and magnesium are then determined in the filtered solution. SMITH AND MCCALLUM[6] suggest the removal of iron, manganese and phosphate before the titration of the alkaline-earth metals with EDTA. COLLIER[7] made a series of photometric analyses to determine the ratio of P/Ca and P/Mg below which there is no interference. He states that "the presence of 3 mg of phosphate as P in 70 ml solution during the titration of 0.1 mg Ca with 0.125*M* EDTA, using murexide as indicator, caused no interference; on the other hand, 1 mg of Mg in 70 ml solution can be titrated in the presence of 1 mg phosphate as P, using Eriochrome Black T as indicator, provided the titration is completed immediately after

TABLE I

TITRATION OF CALCIUM WITH EDTA AT pH 10 IN THE PRESENCE OF PHOSPHATE

Phosphate was added as KH_2PO_4 and calculated as P_2O_5

Expt. No.	*P_2O_5 present mg*	*Ca present mg*	*Ca found mg*	*Difference mg*	*Relative error %*
1	0.2	2.004	1.934	— 0.070	— 3.5
2	0.2	2.004	1.964	— 0.040	— 2.0
3	0.5	2.004	1.917	— 0.087	— 4.4
4	0.5	2.004	1.936	— 0.068	— 3.4
5	0.5	4.008	3.932	— 0.076	— 1.9
6	1.0	4.008	3.800	— 0.208	— 5.2
7	1.0	4.008	3.854	— 0.154	— 3.8
8	2.0	4.008	3.775	— 0.233	— 5.8
9	2.0	4.008	3.709	— 0.299	— 7.5
10	1.0	10.020	9.824	— 0.196	— 2.0
11	1.0	10.020	9.702	— 0.318	— 3.2
12	2.0	10.020	9.486	— 0.534	— 5.3
13	2.0	10.020	9.422	— 0.598	— 6.0

TABLE II

TITRATION OF MAGNESIUM WITH EDTA AT pH 10 IN THE PRESENCE OF PHOSPHATE

Phosphate was added as KH_2PO_4 and calculated as P_2O_5

Expt. No.	*P_2O_5 present mg*	*Mg present mg*	*Mg found mg*	*Difference mg*	*Relative error %*
1	2	1.107	1.090	— 0.017	— 1.5
2	2	1.107	1.100	— 0.007	— 0.6
3	4	1.107	1.100	— 0.007	— 0.6
4	4	1.107	1.099	— 0.008	— 0.7
5	10	1.107	1.078	— 0.029	— 2.6
6	10	1.107	1.086	— 0.021	— 1.9
7	20	1.107	1.078	— 0.029	— 2.6
8	10	2.214	2.156	— 0.058	— 2.6
9	10	2.214	2.170	— 0.044	— 2.0
10	20	2.214	2.112	— 0.102	— 4.6
11	20	2.214	2.050	— 0.164	— 7.4
12	30	2.214	1.839	— 0.375	— 17.0
13	40	2.214	1.890	— 0.324	— 14.6
14	10	5.535	5.520	— 0.015	— 0.3
15	10	5.535	5.520	— 0.015	— 0.3
16	20	5.535	4.061	— 1.474	— 26.6
17	20	5.535	4.330	— 1.205	— 21.8

the NH_4OH–NH_4Cl buffer addition". VERMA, BHUCHAR AND THERATTIL[8] describe a direct chelatometric method for the determination of calcium or magnesium in the presence of phosphate with 1,2-diaminocyclohexanetetraacetic acid (Chenta acid).

EXPERIMENTAL

A series of titrations was carried out in order to determine the minimum concentration of phosphate that can be tolerated in the presence of variable amounts of calcium and magnesium. The results in Tables I and II were obtained by titrating calcium and magnesium with 0.01*M* EDTA at pH 10, using ammonia–ammonium chloride as buffer and Eriochrome Black T as indicator. In all cases the total volume of the solution before the titration was kept the same, about 200 ml. Difficulties were experienced in establishing clear-cut values at which interference began, since its onset appeared to be gradual. In no case was the end-point sharp, especially in the titrations of calcium. In all cases the titrations were carried out immediately after the addition of buffer.

CONCLUSIONS

Table I. Phosphate interferes in the titration of calcium at pH 10 owing to the precipitation of calcium phosphate.

Table II. Phosphate interferes in the titration of magnesium at pH 10, the results obtained being too low. In one exceptional instance (10 mg of P_2O_5 in the titration of 5 mg of magnesium) good results were obtained (Expts. 14 and 15).

Remark. Magnesium phosphate has a tendency to remain in solution in a supersaturated state whereas calcium phosphate does not display such a phenomenon.

DISCUSSION

We thought that the problem of phosphate interference could be solved by adding excess EDTA to the solution of the sample and, after adding buffer, back-titrating the excess with a standard magnesium solution. On trial it was found that the end-point was not sharp and inaccurate results were obtained. Although the addition of EDTA prior to the addition of buffer prevents the precipitation of metal phosphates, yet this precipitation occurs on approaching the end-point in back-titrating the excess of EDTA and this contributes to making the end-point indistinct.

We then thought of adding EDTA as zinc chelate instead of in the free form, in order to dissolve the metal phosphate. As a matter of fact, the addition of zinc-EDTA does not imply adding free EDTA since all the EDTA is present as a chelate with zinc. This would be true if it were not for the fact that the titration is carried out in ammonia–ammonium chloride buffer, in which case ammonia comes into action and partially dissociates zinc-EDTA. The following equilibrium conditions exist in an ammoniacal solution of zinc-EDTA:

$$\text{Zinc-EDTA} \rightleftharpoons Zn^{+2} + \text{EDTA}$$
$$Zn^{+2} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{+2}$$

It was concluded, therefore, that the addition of zinc-EDTA to an ammoniacal solution containing a precipitate of calcium phosphate, is equivalent to the addition of free EDTA and will, likewise, bring about the dissolution of the precipitate; zinc ions are liberated from zinc-EDTA, in a quantity equivalent to the calcium phosphate precipitate that has passed into solution.

This was proved experimentally in the following manner: 10 ml 0.1M solution of zinc chloride was titrated with 0.1M solution of EDTA at pH 10, using ammonia–ammonium chloride buffer and Eriochrome Black T indicator. When this titrated solution, composed of zinc-EDTA, was added to 2 mg of calcium previously precipitated with 30 mg of phosphate at pH 10, it was observed that the precipitate of calcium phosphate gradually dissolved on standing for a few minutes at room temperature.

It was concluded, therefore, that a standard solution of EDTA containing zinc-EDTA would be the appropriate titrant for our purpose. It should be noted that the introduction of zinc ions into the solution to be titrated has the additional advantage of contributing to the sharp end-point met with in all titrations with EDTA using Eriochrome Black T indicator.

Titration of calcium and magnesium with EDTA and Zn-EDTA in the presence of phosphate

Reagents and standard solutions

1. *Standard solution of EDTA 0.01M containing zinc-EDTA 0.05 M.* 4.069 g of zinc oxide (ZnO) are dissolved in a slight excess of hydrochloric acid (about 4 ml) and the total volume is made up to about 200 ml with twice-distilled water. After warming the solution thus obtained, 22.332 g of complexone III (disodium salt of ethylenediaminetetraacetic acid, dihydrate) are added. Concentrated ammonia is then added until the solution becomes clear and the pH has risen to about 8–9. The total volume is then made up to 1 l with twice-distilled water. This solution may be standardized by titration with 0.01M solution of zinc chloride or 0.01M solution of calcium chloride at pH 10, using ammonia–ammonium chloride buffer and Eriochrome Black T indicator.

Remark: Distilled water and ammonia–ammonium chloride buffer contain variable amounts (traces) of metal ions which are titrated at pH 10. This may amount to several drops of 0.01M solution of EDTA per 100 ml of water. To avoid this error and obtain high accuracy, the following modification was applied to all the titrations. To 200 ml of water, 5 ml of ammonia–ammonium chloride buffer and Eriochrome Black T indicator are added. The solution is then titrated with 0.01M solution of EDTA to a blue end-point. To this titrated solution either zinc or calcium chloride solution to be used for the standardization of EDTA is then added.

2. *Ammonia–ammonium chloride buffer.* 670 ml of concentrated ammonia plus 60 g ammonium chloride diluted to 1 l with distilled water.

3. *Eriochrome Black T indicator.* 0.1 g triturated with 10 g of sodium chloride.

Procedure recommended for the titration of calcium and magnesium with EDTA and Zn-EDTA in the presence of phosphate

200 ml of water are introduced into a 500-ml Pyrex Erlenmeyer flask. 5 ml of ammonia–ammonium chloride buffer and a little Eriochrome Black T indicator are added.

The solution is titrated with 0.01M solution of EDTA to a blue end-point. The solution of the sample to be analysed is then added and the solution is immediately titrated with the 0.01M solution of EDTA and Zn-EDTA 0.05M described above. On approaching the end-point, the blue colour slowly turns red; the solution is then allowed to stand for 2–3 min, after which the titration is continued as usual to a persistent blue end-point.

Table III shows some typical results for calcium in the presence of phosphate, obtained according to the above-mentioned procedure.

TABLE III

TITRATION OF CALCIUM WITH EDTA AND Zn-EDTA AT pH 10 IN THE PRESENCE OF PHOSPHATE

Phosphate was added as KH_2PO_4 and calculated as P_2O_5

Expt. No.	*P_2O_5 present mg*	*Ca present mg*	*Ca found mg*	*Difference mg*	*Relative error %*
1	40	2.004	1.998	−0.006	−0.3
2	60	2.004	1.998	−0.006	−0.3
3	20	4.008	3.990	−0.018	−0.4
4	60	4.008	3.990	−0.018	−0.4
5	20	10.020	10.030	+0.010	+0.1
6	40	10.020	9.990	−0.030	−0.3
7	60	10.020	9.990	−0.030	−0.3

CONCLUSION

Calcium (2–10 mg) can be titrated in the presence of phosphate (up to 60 mg) at room temperature, accurate results being obtained.

Table IV shows some typical results obtained for magnesium in the presence of phosphate.

TABLE IV

TITRATION OF MAGNESIUM WITH EDTA AND Zn-EDTA AT pH 10 IN THE PRESENCE OF PHOSPHATE

Phosphate was added as KH_2PO_4 and calculated as P_2O_5

Expt. No.	*P_2O_5 present mg*	*Mg present mg*	*Mg found mg*	*Difference mg*	*Relative error %*	*Titration conditions*
1	60	1.107	1.104	−0.003	−0.3	hot solution
2	20	2.214	2.214	—	—	at room temperature
3	30	2.214	2.187	−0.027	−1.2	at room temperature
4	30	2.214	2.214	—	—	hot solution
5	40	2.214	2.214	—	—	hot solution
6	10	5.535	5.520	−0.015	−0.3	at room temperature
7	20	5.535	4.060	−1.475	−26.6	at room temperature
8	20	5.535	5.520	−0.015	−0.3	hot solution
9	30	5.535	5.520	−0.015	−0.3	hot solution
10	40	5.535	5.520	−0.015	−0.3	hot solution

CONCLUSION

Magnesium can be titrated in the presence of phosphate at room temperature:

(a) when the amount of magnesium does not exceed 5 mg in the presence of not more than 10 mg P_2O_5 (Expt. No. 6).

(b) when the amount of magnesium does not exceed 2 mg in the presence of not more than 20 mg P_2O_5 (Expt. No. 2).

For higher concentrations, the titration should be carried out while the solution is nearly boiling and completed after it has again cooled to room temperature. The reason for this is that at higher concentrations of magnesium and phosphate, precipitation of magnesium phosphate occurs. Unlike calcium phosphate, magnesium phosphate does not dissolve at room temperature during the titration and hence the titration should be performed in a hot solution.

Table V shows some typical results obtained for mixtures of calcium and magnesium in the presence of phosphate.

TABLE V

TITRATION OF CALCIUM AND MAGNESIUM WITH EDTA AND Zn-EDTA AT pH 10 IN THE PRESENCE OF PHOSPHATE

Expt. No.	P_2O_5 *present mg*	*Soln. of Mg 0.01M present ml*	*Soln. of Ca 0.01M present ml*	*Soln. of EDTA 0.01M used ml*	*Relative error %*
1	10	5 (= 1.216 mg Mg)	25 (= 10.02 mg Ca)	30.05[a]	+ 0.2
2	20	5 (= 1.216 mg Mg)	25 (= 10.02 mg Ca)	29.95[a]	— 0.2
3	30	5 (= 1.216 mg Mg)	25 (= 10.02 mg Ca)	30.00[a]	—
4	40	5 (= 1.216 mg Mg)	25 (= 10.02 mg Ca)	29.95[a]	— 0.2
5	50	5 (= 1.216 mg Mg)	25 (= 10.02 mg Ca)	29.95[a]	— 0.2
6	10	10 (= 2.432 mg Mg)	25 (= 10.02 mg Ca)	35.00[a]	—
7	20	10 (= 2.432 mg Mg)	25 (= 10.02 mg Ca)	35.00[b]	—
8	30	10 (= 2.432 mg Mg)	25 (= 10.02 mg Ca)	34.95[b]	— 0.1
9	40	10 (= 2.432 mg Mg)	25 (= 10.02 mg Ca)	34.95[b]	— 0.1
10	50	10 (= 2.432 mg Mg)	25 (= 10.02 mg Ca)	34.95[b]	— 0.1

[a] Titration at room temperature. [b] Titration of a hot solution.

CONCLUSION

Magnesium and calcium, when present together, can be titrated in the presence of phosphate, within the permissible range of quantities at the right temperature, as follows:

(a) Titration at room temperature:

(1) 2–10 mg calcium in the presence of not more than 60 mg P_2O_5.
(2) 1 mg magnesium in the presence of not more than 50 mg P_2O_5.
(3) 1–2 mg magnesium in the presence of not more than 20 mg P_2O_5.
(4) 2–5 mg magnesium in the presence of not more than 10 mg P_2O_5.

(b) Titration of hot solutions:

2–5 mg magnesium in the presence of not more than 50 mg P_2O_5.

ACKNOWLEDGEMENT

The authors are indebted to Dr. A. BANIEL, chief chemist of Israel Mining Industries Laboratories, for his personal interest in the progress of the work and for permission to publish this paper.

SUMMARY

The authors have developed a rapid and accurate volumetric method for the determination of small quantities of calcium and magnesium with EDTA in the presence of phosphate.

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Received March 6th, 1958

POSTPRECIPITATION OF ZINC WITH HOMOGENEOUSLY PRECIPITATED COPPER SULFIDE

by

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INTRODUCTION

Even though the (copper sulfide) - (zinc ion) system has been investigated fairly thoroughly[1], there remains disagreement as to how zinc ions are precipitated with the copper sulfide. Early authors viewed the phenomenon as inner adsorption or as coordination-compound formation[2,3], but recent work shows it to be postprecipitation[1]. It is generally agreed now that the amount of zinc found with the copper sulfide increases with rapidity of precipitation, age of the precipitate, digestion time, digestion temperature, and shaking, and decreases with increasing acid concentration[1,4]. KOLTHOFF AND PEARSON[1] suggest that postprecipitation is due to a finely divided state of copper sulfide which adsorbs hydrogen sulfide, which in turn reacts somehow with the zinc ion. CALDWELL AND MOYER[5] found that organic substances of the type R-CH=CH-CHO reduced the postprecipitation considerably. SUGIMOTO, HOSHI, AND KURIBAYASHI[6] suggest that the phenomenon is due to a chain reaction. RUDNEV[7] points out that the differences of opinion are probably due to the widely varying conditions employed by persons investigating this system.

MOSER[8] first employed homogeneous precipitation to form denser precipitates; IWANOV[9] first reported thioacetamide as a general analytical reagent; and FLASHKA[10] then took the lead in using it as a source of sulfide for cation precipitations. AMIN[11] studied the precipitation of copper using thioacetamide and recommended a threefold excess of thioacetamide, heating it in a boiling water bath for 5 min, filtration, and then solution of the excess thioacetamide in dilute nitric acid.

In this present work, the coprecipitation of zinc ion with copper sulfide which has been precipitated from homogeneous solution using thioacetamide has been investigated. Zinc determination has been facilitated by labelling with radioactive ^{65}Zn. Variables which have been studied include: amount of thioacetamide, amount of zinc, time, temperature, acid concentration, and blocking of the precipitate surface.

EXPERIMENTAL PROCEDURE

Chemicals and apparatus

^{65}Zn with a specific activity of 75 mC/g as zinc chloride was obtained from Oak Ridge National Laboratory. This was added to reagent zinc sulfate solutions to produce labelled solutions with final concentrations of 2.5, 10, and 25 mg zinc per ml. A reagent copper sulfate solution containing 12.5 mg copper per ml was also prepared. The thioacetamide was Eastman White Label. All other chemicals were of reagent-grade quality.

Procedure

For each experiment, 2.00 ml copper solution (containing 25 mg copper), 1.00 ml zinc solution (containing 2.5, 10, or 25 mg zinc), 1.00 ml thioacetamide solution (containing 30, 50, or 100 mg thioacetamide), and 1.00 ml hydrochloric acid solution of known concentration were pipetted into a 10-ml test tube fitted with a condenser. In some cases, some of these were omitted; in other cases, other substances were added. The final volume was then brought to 5.00 ml. The test tube was then placed in a water bath at an appropriate temperature (80°, 90°, or 98°) for an appropriate time (10–180 min). It was removed, the precipitated copper sulfide was filtered and washed, then dissolved in hot nitric acid. Both the combined filtrate and washings and the dissolved precipitate solution were diluted to 10.00 ml. The solutions were then sampled with a 100-λ pipet, the aliquots placed on planchets, dried, and counted for radioactivity. All filtrates were tested for completeness of precipitation of the copper.

For each set of determinations under given conditions, at least four experiments were performed. The mean value was determined and the standard deviation was calculated.

RESULTS

Several experiments were performed using only zinc sulfate, thioacetamide, and hydrochloric acid to see if the solubility of zinc sulfide was being exceeded in the range of acid concentrations (0.1–2.0N) used in this investigation. In some cases charcoal was added to provide nuclei for condensation[1]. Results of these studies showed that the solubility of zinc sulfide was not being exceeded.

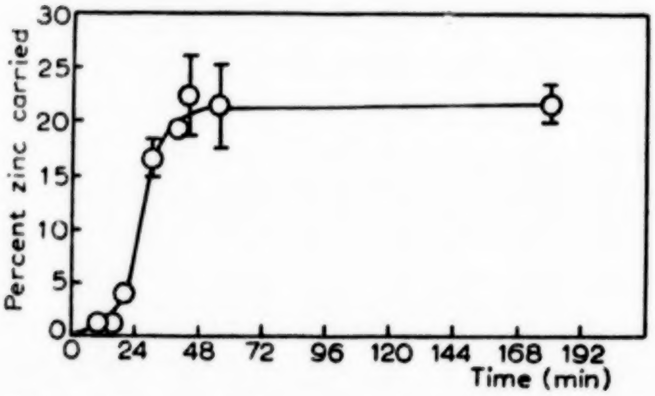

Fig. 1. Per cent zinc carried as a function of time. Conditions: 25 mg Cu, 2.5 mg Zn, 50 mg thioacetamide, 0.1N HCl, 98°.

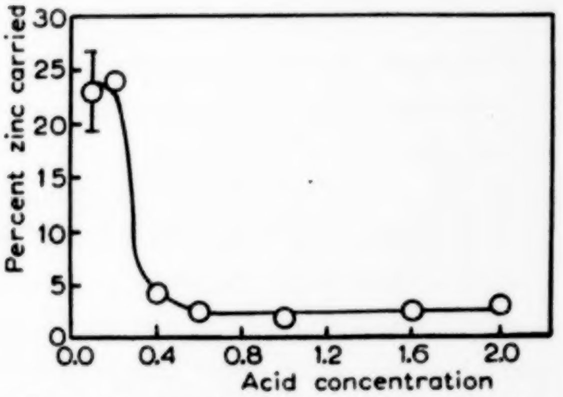

Fig. 2. Per cent zinc carried as a function of acid concentration. Conditions: 25 mg Cu, 2.5 mg Zn, 50 mg thioacetamide, 45 min, 98°.

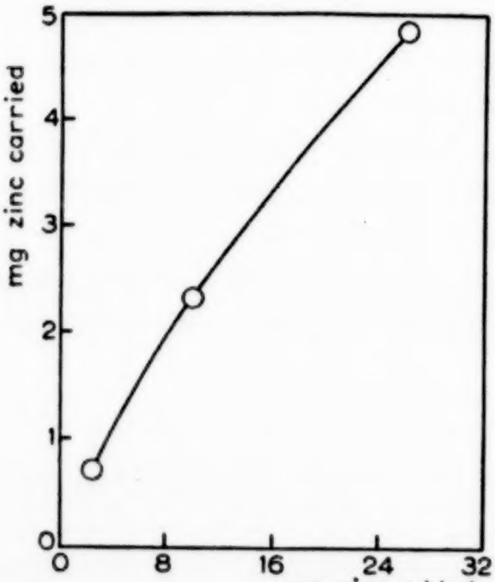

Fig. 3. Mg zinc carried as a function of mg Zn added. Conditions: 25 mg Cu, 50 mg thioacetamide, 0.1N HCl, 45 min, 98°.

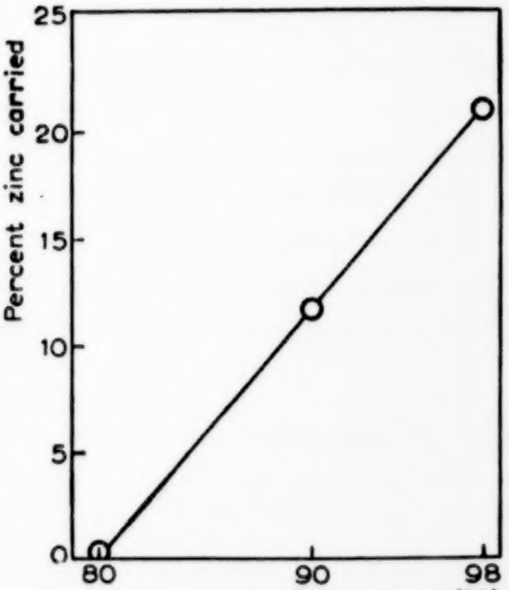

Fig. 4. Per cent zinc carried as a function of digestion temperature. Conditions: 25 mg Cu, 2.5 mg Zn, 50 mg thioacetamide, ~~0.1N HCl~~, 60 min.

Fig. 1 is a typical curve showing the relation of per cent zinc co-precipitated as a function of time. Similar curves were obtained when the amount of zinc was changed to 10 or 25 mg, when the amount of thioacetamide was changed to 100 mg, when the acid concentration was changed to 0.3 or 1.0*N*, or when the temperature was changed to 80° or 90°. Fig. 2 is a typical curve showing the relation of per cent zinc coprecipitated as a function of acid concentration. Similar curves were obtained when the amount of zinc was changed to 10 or 25 mg, when the amount of thioacetamide was changed to 100 mg, when the time was changed to 90 or 180 min, or when the temperature was changed to 80° or 90°.

Fig. 3 is a typical curve showing the relation of mg zinc coprecipitated as a function of mg zinc added. Similar curves were obtained for 100 mg thioacetamide or for 90 or 180 min. Fig. 4 is a typical curve showing the relation of per cent zinc coprecipitated as a function of digestion temperature. Similar curves were obtained for 10 or 25 mg zinc, for 100 mg thioacetamide, for 0.3*N* acid, or for 90 or 180 min digestion time.

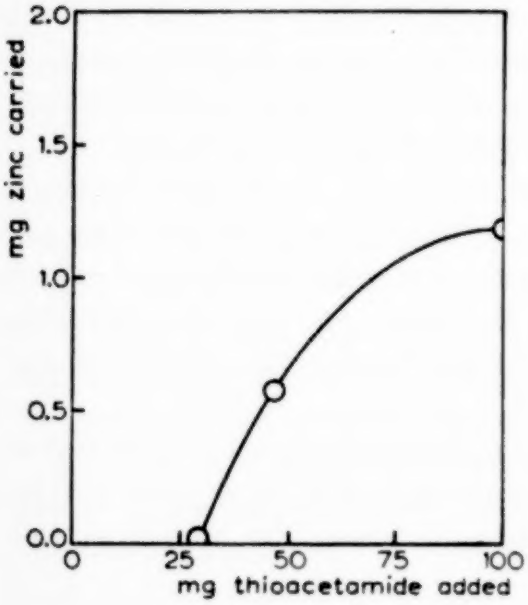

Fig. 5. Mg zinc carried as a function of mg thioacetamide added. Conditions: 25 mg Cu, 2.5 mg Zn, 0.1*N* HCl, 60 min, 98°.

Fig. 5 is a curve showing the relation of mg zinc coprecipitated as a function of mg thioacetamide added.

Several special sets of experiments were performed to help elucidate the coprecipitation process. (1) In one, 25 mg copper was precipitated in 0.1*N* hydrochloric acid with 50 mg thioacetamide digested at 98° for 20 min. This precipitate was filtered off and washed with 5*N* hydrochloric acid. It was then suspended in 10 ml 0.1*N* hydrochloric acid to which 2.5 mg zinc had been added and allowed to digest at 98° for 60 min. Five such experiments showed 3 ± 1% of the zinc coprecipitated. (2) In another set of experiments, the same procedure was followed except that the precipitates were not washed. Five experiments showed 17 ± 2% of the zinc coprecipitated. (3) In a third set of experiments, 25 mg copper was precipitated as in the second set. Then the precipitate was digested for 60 min at 98° in 10 ml of a solution made up from 3 ml saturated hydrogen sulfide solution, 0.1*N* in hydrochloric acid, and containing 2.5 mg zinc. Five experiments showed 40 ± 4% of the zinc coprecipitated. (4) In a fourth set of experiments, the procedure of the third set was followed except that the digestions were carried out in sealed tubes to prevent hydrogen sulfide from escaping.

Five experiments showed 44± 3% of the zinc coprecipitated. (5) In a fifth set of experiments, 25 mg copper, 2.5 mg zinc, 100 mg thioacetamide, and 256 mg crotonaldehyde in 0.1*N* HCl were digested for 60 min at 100°. Five experiments showed 1.0 ± 0.7% of the zinc coprecipitated.

DISCUSSION

The amount of zinc coprecipitated in these studies (a) increases with time up to about 45 min after which it remains constant, (b) decreases with acid concentration up to about 0.4*N* after which it remains constant, (c) increases with original zinc concentration, (d) increases with digestion temperature, and (e) increases with thioacetamide concentration.

All of these observations could be explained by a process involving the adsorption of bisulfide ions on the surface of the copper sulfide, and the subsequent attraction of zinc to these adsorbed entities. Observation (a) shows that the process is one of postprecipitation. Observation (b) may be explained by realizing that the concentration of bisulfide ions decreases as the acid increases. Observation (c) is a result of mass action. Observation (d) may be related to the well-known fact that slower precipitation which takes place at lower temperatures gives precipitates with smaller surface areas[1]. Observation (e) shows the result of increasing hydrogen sulfide concentration.

The special sets of experiments may be interpreted as follows. The results obtained in sets (1) and (2) indicate that washing removes the adsorbed bisulfide and thus decreases the carrying. The results from sets (3) and (4) show that the addition of excess hydrogen sulfide produces more adsorbed bisulfide and thus increases the carrying. The results from set (5) indicate that carrying is decreased when the surface of the precipitate is coated[5].

In general, the per cent zinc carried with copper sulfide precipitated from homogeneous solution was much less than that precipitated using gaseous hydrogen sulfide. The main reason is probably the smaller surface area presented by copper sulfide precipitated from homogeneous solution.

SUMMARY

The postprecipitation of zinc ion onto copper sulfide which has been precipitated from homogeneous solution using thioacetamide has been investigated under various conditions. The zinc carried increases with increasing time, increasing concentration of zinc, increasing digestion temperature, increasing thioacetamide added, and decreasing acid concentration. On the basis of these and several other special observations, it is believed that the postprecipitation is a result of adsorption of bisulfide ion on the surface of the copper sulfide, this adsorbed layer then reacting with the zinc ion.

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Received March 11th, 1958

THE SEPARATION OF FLUORIDE IONS FROM INTERFERING ANIONS AND CATIONS BY ANION EXCHANGE CHROMATOGRAPHY

by

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INTRODUCTION

Most methods of determining fluoride are subject to serious errors when ions such as calcium, barium, ferric iron, aluminium, phosphate and sulphate are present, and a preliminary separation of fluoride from them is usually necessary. The method proposed by WILLARD AND WINTER[1] involving the distillation of fluoride as fluorosilicic acid is still widely used, but it is time-consuming and sometimes gives inaccurate results. Recently, interfering cations have been removed by exchange on a cation-exchange resin[2,3], and phosphate and fluoride have been separated by paper chromatography[4] and by anion exchange chromatography[4,5]. Usually interfering anions and cations are both present and their removal by published ion exchange techniques requires two exchange operations. This increases the manipulative errors and the time required for the analysis, and is little improvement upon WILLARD-WINTER distillation.

As a result of the present investigation, a method is proposed for the removal together of the interfering cations and anions in a column containing a strongly-basic anion exchange resin. The cations are converted into complex anions which are strongly held on the resin, while fluoride ions, which are only weakly adsorbed, are quantitatively eluted from the column.

Ethylenediaminetetraacetic acid (EDTA) was found to be a suitable reagent for complexing the cations, since it reacts with a wide range of metals which interfere with fluoride determinations, to form stable chelate compounds which are water-soluble and negatively charged. The use of EDTA has the further advantage that substances normally insoluble at the high pH used are maintained in solution.

The proposed method has been used to determine fluorine in several mineral calcium phosphates (rock phosphates) which contain 0.5–4.3% F and appreciable quantities ($\sim$1%) of aluminium, iron and magnesium, and it can probably be extended to the determination of fluorine in substances requiring a preliminary fusion with sodium carbonate.

APPARATUS

A Locarte Automatic Fraction Collector, Model LCD/3, was used in the preliminary experiments, the photoelectric drop-counter enabling a series of equal volumes to be collected from the resin column. The titration of fluoride was carried out in a 4-cm cell of an EEL Absorptiometer, with stirring after the addition of each incremental volume of titrant.

Preparation of columns. The construction and dimensions of the columns are shown in Fig. 1. Under free drainage, there was always liquid in the bed volume and no tap on the outlet was necessary. Three columns were constructed enabling triplicate determinations to be carried out simultaneously.

The resin De-Acidite FF (manufactured by the Permutit Co. Ltd.,) was supplied in the size fraction $-16 + 50$ B.S.S.; it was air dried and ground to the size fraction $-60 + 100$ B.S.S. Fine material still adhering to the resin particles was removed by washing several times with distilled water and decanting the liquid after the resin had settled. When the supernatant liquid was clear, the resin was stirred first with *N* hydrochloric acid, and after washing, with *N* sodium hydroxide; this alternating treatment was repeated three times. A suspension of the resin in water was poured into vertically-clamped columns and allowed to settle for several hours; the final level of resin is shown in Fig. 1 and any excess was removed. Under free drainage, the liquid level just fell to the top of the retaining glass wool, and this gave the most efficient column operation. The columns were treated alternately with *N* sodium hydroxide (50 ml) and *N* hydrochloric acid (50 ml) until the effluent was clear, and after the final acid treatment, the columns were washed with distilled water. Before use, 50 ml of elutriant solution were run through.

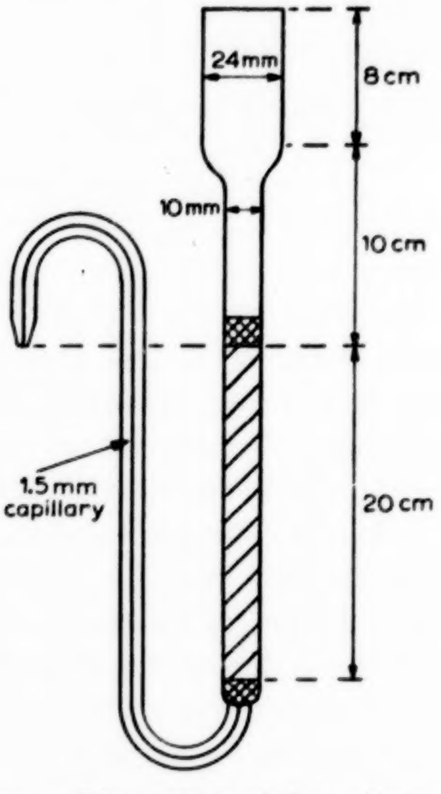

Fig. 1. Dimensions of the column.

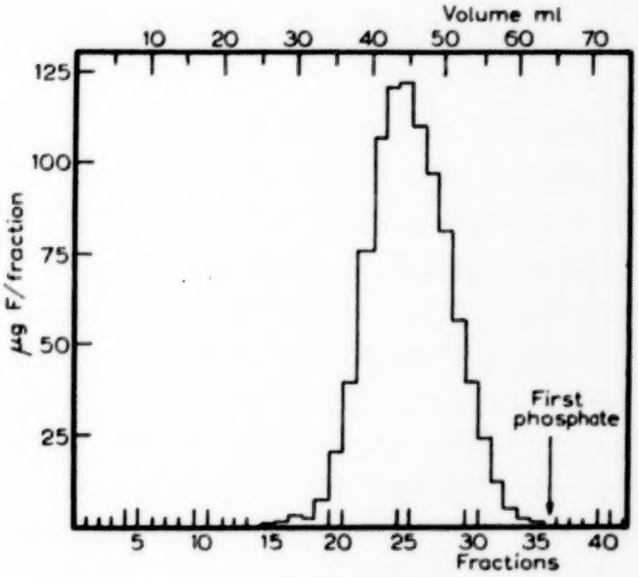

Fig. 2. Elution of 0.05 mmoles sodium fluoride and 0.30 mmoles sodium dihydrogen phosphate. Elutriant: 0.05*M* ammonium chloride buffered at pH 8.8 with ammonia.

After completion of the experiment, the columns were regenerated with *N* hydrochloric acid (50 ml) and after washing, with elutriant solution (50 ml).

PRELIMINARY EXPERIMENTS

Some trial experiments were conducted to determine the conditions suitable for eluting fluoride quantitatively from an anion column while retaining phosphate and EDTA chelates on the resin. Factors which affect this separation are the ionic form of the resin, and the pH and concentration of the elutriant solution. If the resin is used in the chloride form, which is intermediate in stability between the fluoride form and the phosphate form, an elutriant solution containing chloride ions should remove the fluoride quantitatively, leaving the phosphate and EDTA chelates adsorbed on the column. A high pH should enhance this separation as the larger charge on the polyvalent ions increases their affinity for the resin, whereas the fluoride adsorption is relatively little effected.

Experiment 1. A solution containing 0.05 mmoles NaF and 0.30 mmoles NaH_2PO_4 was added to a column prepared as described above, and eluted with 0.05*M* ammonium chloride buffered at pH 8.8 with ammonia; the effluent solution was collected in a number of fractions. Each fraction was analysed quantitatively for fluoride using an absorptiometric method which depends on the decomposition of an aluminium-quinalizarin sodium sulphonate complex[6], and qualitatively for phosphate by the method of TRUOG AND MYER[7]. Fig. 2 shows that a complete separation of phosphate and fluoride was just achieved, the fluoride being eluted in fractions 15 to 35, and the first phosphate being detected in fraction 36.

Experiment 2. A sample of calcium fluoride was dissolved in hydrochloric acid, slightly more disodium EDTA added than was required to complex the calcium, and the solution made alkaline with ammonia solution. Under these conditions the fluoride remained in solution, and an aliquot containing about 6.5 µmoles CaF_2 was added to the column.

After elution with 0.05*M* ammonium chloride-ammonia buffer at pH 8.8, the fractions collected were analysed as before for fluoride. Calcium could not be detected by flame photometer in any of the fractions and the fluoride was quantitatively eluted in the same fraction of effluent as in the first experiment.

Experiment 3. A solution of a sample of Gafsa rock phosphate was prepared in the same manner as for calcium fluoride, and an aliquot was eluted with 0.05*M* ammonium chloride-ammonia buffer at pH 8.8 as in the previous experiments. No phosphate or EDTA could be detected in any of the fractions and fluoride was eluted in the same effluent volume as in the two previous experiments.

These experiments showed that fluoride could be satisfactorily separated from phosphate and metal-EDTA chelates by simple anion exchange chromatography, and form the basis of the method described in the next section for the determination of fluorine in rock phosphates. The elutriant solution was diluted to 0.025*M* and its pH increased to 9.2 to increase the separation of phosphate and fluoride.

When these experiments were largely completed, ZIPKIN, ARMSTRONG AND SINGER[4] published a procedure for separating fluoride and phosphate by anion exchange chromatography under slightly different conditions. Using the hydroxyl form of a strongly basic resin for adsorption, and eluting with 0.5*N* sodium hydroxide, they achieved a quantitative separation for fluoride from phosphate. These conditions could also be applied to the method described below, though the high concentration of electrolyte might make estimation of the fluoride in the effluent more difficult.

ESTIMATION OF FLUORINE IN MINERAL PHOSPHATES

Fluorine was determined by titration with thorium nitrate solution using alizarin red S as the indicator and buffering the solution at pH 2.9 with half neutralized monochloracetic acid; the end-point was difficult to observe visually and was obtained absorptiometrically. The end-point depended on the dilution, and reproducible results could only be obtained when the volume at the end-point of each titration was approximately the same[8]. A prior knowledge of the end-point was therefore necessary so that the volume of the solution could be adjusted with distilled water before beginning the titration. When the equivalent of the titrant and the approximate amount of fluoride present were known, the end-point could be calculated with sufficient accuracy; otherwise a preliminary titration was necessary with no adjustment of volume.

The reaction was not stoicheiometric and a calibration curve was prepared; this was found to be linear within experimental error over the range 10.6 to 53 µg fluoride, and re-calibration of the reagent after one month yielded an almost identical line.

The chloride content of the effluent solution was not found to interfere with the titration of fluoride by thorium nitrate.

Reagents

Elutriant solution. Dissolve 53.5 g A.R. ammonium chloride in 800 ml distilled water and adjust to pH 9.2 with 0.880 A.R. ammonia using a pH meter; dilute to 1 l. Dilute 25 ml of this stock solution to 1 l to give an elutriant solution 0.025*M* in ammonium chloride.

Alkaline EDTA solution. Dissolve 93 g disodium ethylenediaminetetraacetate dihydrate in 60 ml 0.880 A.R. ammonia and dilute to 250 ml. This solution is approximately M in EDTA and $4N$ in ammonia.

Normal hydrochloric acid. Dilute 86 ml A.R. hydrochloric acid (36%) to 1 l.

0.1N monochloracetic acid. Dissolve 10 g A.R. monochloracetic acid in 1 l distilled water.

Indicator solution. Dissolve 0.01 g alizarin red S (sodium alizarin sulphonate) in 100 ml distilled water.

Thorium nitrate solution. Dissolve 2.94 g A.R. thorium nitrate ($Th(NO_3)_4.6H_2O$) in 1 l distilled water acidified with 0.4 ml A.R. nitric acid. Dilute 100 ml of this stock solution to 1 l for titration, to give a solution $5 \cdot 10^{-4} M$.

Standard fluoride solution. Recrystallize sodium fluoride from hot distilled water, dry at 105°, and store in a desiccator over calcium chloride. Estimate the fluoride content by precipitation as lead chlorofluoride using the procedure described by VOGEL[9]. Weigh out accurately about 0.21 g recrystallized sodium fluoride and dissolve in 200 ml distilled water; dilute 25 ml of this stock solution to 500 ml to give a solution containing about 24 µg F per ml.

Method

Weigh not more than 0.2 g rock phosphate into a 250-ml beaker, cover with a clock glass, and add 6 ml N hydrochloric acid; leave for 24 h with occasional stirring. Heat must not be used to assist dissolution of the phosphate as fluorine may be lost. Add 3 ml alkaline EDTA solution and warm the liquid to about 70° for a few minutes. After cooling rinse down the sides of the beaker and the clock glass, and filter the liquid through a 15-cm Whatman 42 filter paper into a 250-ml standard flask. Wash the beaker and filter three times with distilled water and make the solution up to volume.

Pipette an aliquot (10 ml) of this solution into a column prepared as described above and when this has run through, wash with 10 ml distilled water. Add $0.025M$ elutriant solution to the column and after rejecting the first 15 ml, collect 100 ml of effluent solution in a standard flask; this volume contains all the fluorine in the aliquot added to the column. Titrate 10 ml of effluent with $0.1M$ monochloracetic acid using bromo-thymol blue as the indicator until one drop of acid just turns the solution yellow. Pipette 40 ml of the effluent solution into a 50-ml standard flask, add a volume of monochloracetic acid equal to eight times the titre of the 10-ml aliquot and make the solution up to the mark.

Pipette 15 ml of the buffered effluent, 1 ml of alizarin indicator and enough distilled water to make the volume at the end-point up to 22 ml into a 4-cm cell of an EEL Absorptiometer. Add equal volumes (*e.g.* 0.20 ml) of $0.0005M$ thorium nitrate solution from a semi-micro burette, and after stirring, measure the absorption of the solution against water, using an Ilford filter No. 604 (absorption maximum at about 520 mµ). When the absorption begins to increase rapidly, reduce the volumes of titrant added and continue the titration until the change in absorption after each addition of titrant becomes small. Plot the increase in absorption per ml for each incremental volume ($\Delta A/\Delta V$) against the volume of titrant used; this curve will show a maximum value at the end-point. Repeat the titration with two further aliquots of the buffered effluent.

Determine the equivalent of the thorium nitrate titrant by standardization against buffered sodium fluoride solutions. Pipette 30-ml aliquots of $0.025M$ elutriant solution into 50-ml standard flasks containing 0, 1.5, 3.0, 4.5, 6.0, and 7.5 ml standard sodium fluoride solution. Titrate 10 ml of elutriant solution with monochloracetic acid using bromo-thymol blue as the indicator, and add six times the titre to each flask, finally making the solutions up to volume. Titrate 15-ml aliquots with the thorium nitrate solution using the absorptiometer as before, and prepare a calibration curve.

If the fluoride in the final aliquot of buffered effluent solution is equivalent to V ml of sodium fluoride solution of molarity m, and W is the weight in grams of the sample, then the percentage of fluorine in the rock phosphate is $396\ mV/W$.

RESULTS AND DISCUSSION

The method described was used to determine fluorine in three rock phosphate samples. Each sample was analysed in triplicate using different sample weights and the results obtained are given in Table I. The figures for percentage fluorine in the sample do not show any noticeable trend as the sample weight is increased and the deviations

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TABLE I

RECOVERIES OF FLUORIDE FROM MINERAL PHOSPHATES

Phosphate sample	*Weight of sample* g	*Fluoride recovered* mg*	*Fluoride in sample* %*
Rock phosphate	0.0707	2.94 ± 0.05	4.16 ± 0.07
From Morocco	0.1400	5.96 ± 0.12	4.26 ± 0.09
	0.2000	8.24 ± 0.20	4.12 ± 0.10
Fluorapatite	0.0691	2.40 ± 0.05	3.47 ± 0.07
From Ontario	0.1411	4.86 ± 0.10	3.44 ± 0.07
	0.1996	6.94 ± 0.17	3.48 ± 0.09
Rock phosphate	0.0703	2.50 ± 0.08	3.56 ± 0.11
From Tennessee **	0.1418	5.15 ± 0.12	3.63 ± 0.08
	0.2015	7.16 ± 0.12	3.55 ± 0.06

* Errors quoted are for uncertainty in the end-point of the titration.

** National Bureau of Standards Standard Sample No. 56; JACOB AND REYNOLDS found 3.56% fluoride in this sample[10], and WILLARD AND WINTER found 3.47 and 3.50%[1].

from the arithmetic mean are accounted for by the uncertainty in determining the end-point of the titration. There are therefore no apparent additive errors in the procedure.

The Bureau of Standards Tennessee rock phosphate (standard sample No. 56) was analysed by WILLARD AND WINTER in their original work[1], and earlier by JACOB AND REYNOLDS[10] after distillation of the contained fluorine as silicon tetrafluoride; these analyses are also given in Table I. The results obtained with the procedure described here are slightly higher than these earlier analyses, but when the error in the titration is taken into account, the difference is not significant.

These results show that the proposed separation procedure is quantitative and that it introduces no errors which are detectable with the titration of fluoride by thorium nitrate. The method is flexible within limits and Fig. 3 shows that if 20 ml of sample

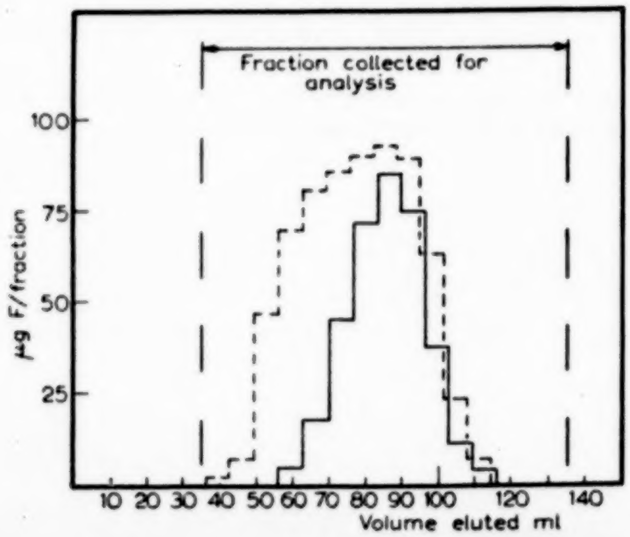

Fig. 3. Elution of aliquots of EDTA solution of Moroccan rock phosphate. Elutriant 0.025 M ammonium chloride buffered at pH 9.2 with ammonia. —— 10-ml aliquot; — — — 20-ml aliquot. No phosphate in any fraction.

solution is added to the column instead of the usual 10 ml, the fluoride content is eluted in the same fraction of effluent. This allows a certain latitude in the experimental procedure to suit the amount of fluoride present. However, there is a maximum of about 1 mg of fluoride which can be adequately separated from phosphate and EDTA chelates with the size of column described, and this limits the methods which can be used to determine fluoride in the effluent to absorptiometric methods, micro-titration, and possibly precipitation by triphenyl tin chloride, for which the quoted range is 0.1–50 mg fluoride per 20–100 ml[11].

Although the method is at present limited to circumstances where the fluoride present in the sample is soluble in alkaline EDTA, there is little difficulty in principle in extending it to those substances for which a preliminary fusion with sodium carbonate is necessary. At the high pH used, carbonate will be strongly adsorbed on the resin and fluoride should be quantitatively eluted, although it may be necessary to increase the size of column to ensure adequate separation. Thus the removal of interfering substances from fluoride solutions by anion exchange chromatography promises to be a generally applicable alternative to WILLARD-WINTER distillation, and in the determination of fluorine in mineral rock phosphates is accurate and extremely simple to use.

SUMMARY

Fluoride may be separated from phosphate and the anionic metal chelates of ethylenediaminetetraacetic acid (EDTA) by absorption on, and elution from, an anion exchange column containing a strongly basic resin. This provides a simple and accurate method of removing interfering ions prior to the determination of fluoride by thorium nitrate titration, and is a satisfactory alternative to WILLARD-WINTER distillation. A procedure is described for the determination of fluorine in rock phosphates and other materials soluble in alkaline EDTA solution.

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Received March 7th, 1958

ELECTROSTATIC DISCHARGE METHODS OF ZONE LOCATION FOR PAPER CHROMATOGRAPHS

III. FURTHER DEVELOPMENTS

by

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Since the writer introduced this new modality in 1957[1] work on the applications of the electrostatic discharge principle has continued and the results obtained are described in the present paper.

In part II[1] the grid cut-off for the anode current depended for its electron supply upon those emitted from the valve filament. Because the blank portions of the chromatograph caused a small leakage as they crossed the electrodes of the zone locator, a zero-shunt circuit was employed to set back the meter reading to zero for the filter paper before location was commenced. Under the requirements of this new technique the zone locator is employed only for discovering the zones and it is not essential therefore for the valve to operate on the straight portion of its characteristic curve.

Fig. 1. illustrates alternative schemes which not only dispose of the zero-shunt and

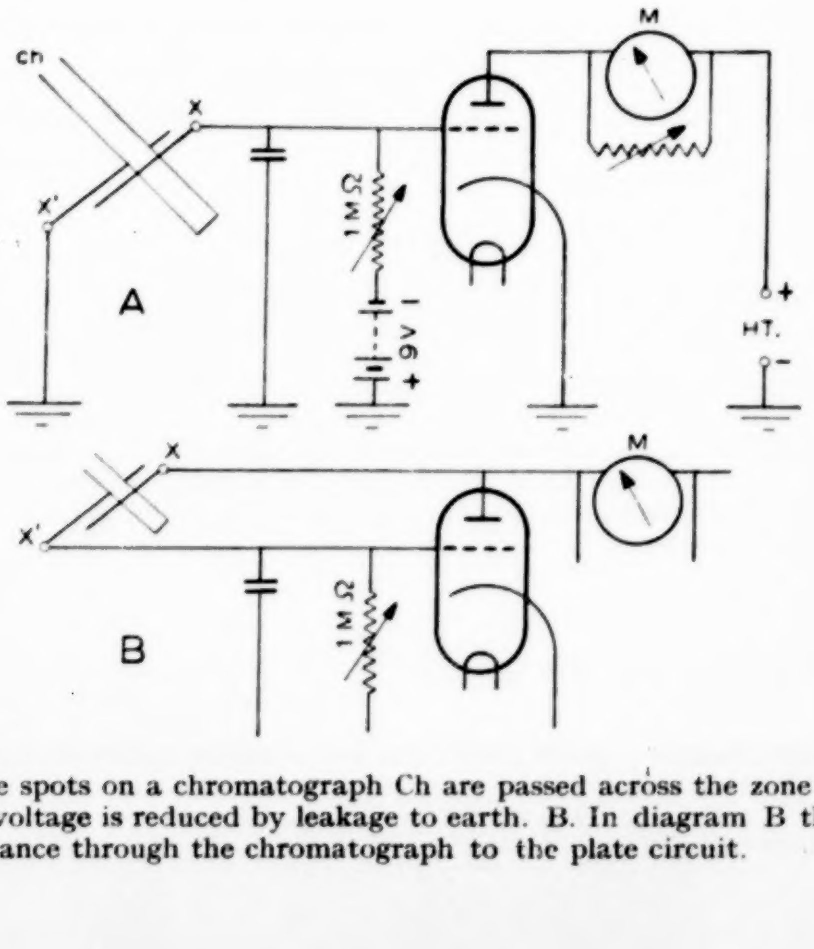

Fig. 1. A. When the spots on a chromatograph Ch are passed across the zone locator electrodes X and X′ the grid voltage is reduced by leakage to earth. B. In diagram B the grid voltage is lowered by conductance through the chromatograph to the plate circuit.

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ensure a complete grid cut-off but also enable almost any type of triode to be used.

Both of these circuits have been tested and they both operate equally well. In Fig. 1A the grid is supplied the additional negative charge by means of a 9 V grid bias battery with its positive terminal connected to earth and its negative terminal connected through a 1-megohm resistor to the grid.

The passage of a zone or spot across the electrodes X and X′ removes electrons from the grid and an anode current is registered by the milliammeter M.

Fig. 1B is the alternative circuit. In this case instead of reducing the negative charge on the grid by leakage to earth the charge is reduced by a positive EMF obtained from the anode circuit.

Automatic spot or zone location

The writer has recently designed and constructed an automatic zone locator which not only locates both visible and invisible conductive spots but underlines each one from edge to edge as it passes the electrodes of the locator.

Briefly the scheme is as follows:

As soon as the forward edge of a spot commences to bridge the electrodes the anode current operates a relay. This in turn causes a magnet to press a graphite pencil (located under the chromatograph) against its underside where it continues to mark a pencil line until the further edge of the spot passes from the electrodes and the relay goes out of action.

It was a surprise to the writer to find that the exceedingly small quantity of solute at the extreme edge of a spot provided sufficient conductance to operate a relay reliably.

It was decided therefore to discover the order of resistance met with at the edges of the spots. A number of circular spots (2 cm in diameter) of an aqueous solution of $N/128$ $CuCl_2$ was deposited

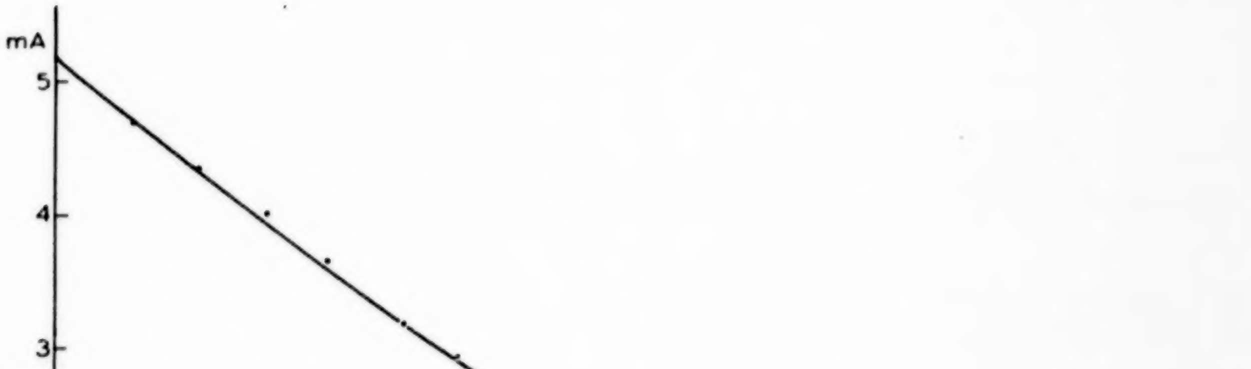

Fig. 2. This resistance–anode current graph was prepared from anode current measurements when variations of resistance (in steps of 40 megohms) were substituted for a spot by connection across the electrodes of the zone locator. Plate voltage 100, resistance from point to point on graph 80 megohms. 0–10 milli-amp. scale of multi-meter used for all readings.

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on a strip of filter paper. Each spot contained (when spread over its entire area) only 0.025 mg of that solute. After drying all night the extreme edges of each spot when bridged across the electrodes of the locator gave a milliampere reading of approximately 0.7.

From the resistance-anode current graph (see Fig. 2) we see that this represents about 1400 megohms. It is obvious therefore that we have a means for detecting an extremely small amount of conductance even when we require the process to be automatic. If the zone location is conducted by an operator visually, only a very slight movement of the meter needle will be sufficient and we can then locate even smaller quantities or the apparatus can be employed to locate much less conductive substances.

Quantitative measurements

The writer finds the following technique takes less time than the area measurement method used with his R.Rf. method of zone location[2] and as the use of a planimeter is avoided there is less possibility of human error.

After location the spots or zones are exised and each zone is dissolved in a measured volume 'X' of the solvent. A sample of each zone solution is then examined for conductance by means of a titrimeter (or solution comparator)[3,4], and a meter deflection obtained. After a chemical test to ascertain the nature of the solute, small measured quantities of that solute are added from stock to a comparatively large measured volume of the original solvent until the meter deflection of the titrimeter agrees with that obtained for 'X'. Both concentrations are then the same, and the amount of solute in 'X' is readily calculated. Up to the present only a small number of solutes have been tested. All electrolytes are detectable, also some organic substances such as imidazole whereas fatty acids are not.

The problem of variations in atmospheric humidity

When parts I and II[1] were written, the valve of the zone locator was operated at a fixed voltage, and on days when the chromatograph was too dry it was exposed to steam before location.

The writer has devised a better method *viz.*: Instead of altering the humidity of the filter paper to suit the anode voltage a better scheme is to alter the voltage to suit prevailing conditions. During the present tests the atmospheric humidity has varied between 55% and 96%.

SUMMARY

This paper (which is a continuation from Parts I and II) shows that by the application of a suitable negative grid bias through a swamping resistor, any type of triode may be employed in the Chromatograph circuit of BLAKE's electrostatic zone locator.

By the inclusion of a relay (which operates an electromagnetic marking device) in the anode circuit of the valve, the zone locator works automatically as the chromatograph is pulled across the electrodes by means of a small motor. Each zone or spot is underlined automatically and leaves the locator ready for excision and analysis by solution comparison.

--It is shown by a resistance-anode current graph that the resistance at the extreme edges of a spot of $CuCl_2$ is of the order of 1400 megohms which as the electrodes are bridged operates the relay satisfactorily.

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Received March 25th, 1958

PAPER CHROMATOGRAPHY IN THE SEPARATION OF IONS. IV

by

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From a solvent consisting of acetone, water and hydrochloric acid, MAJUMDAR AND CHAKRABARTTY[1] successfully separated individual ions into distinct bands from mixtures of at least seven common ions.

The same solvent was found effective for the separation of five of the precious metals[2] from their respective mixtures and of the same number of elements of the copper, silver and arsenic groups[3].

This paper records a systematic study by ascending paper chromatography of the separability from each other of the alkali metals, alkaline earth metals, IIIA and IIIB group elements and some anions, such as phosphate, arsenate, vanadate, tungstate, molybdate and chromate, with the solvent consisting of *tert.*-butyl alcohol, water, hydrochloric or acetic acid, with or without complexing agents.

EXPERIMENTAL

The apparatus used and the procedure adopted were the same as described earlier[1]. The test solutions of cations were prepared from the nitrates of the respective metals except those of titanium and zirconium, where chloride solutions were used. Solutions of niobium and tantalum were prepared from their pentoxides, which were fused with potassium bisulphate and extracted with an ammonium oxalate solution. The solutions of anions were prepared from the ammonium salts of vanadate, molybdate and phosphate, and from the sodium salts of arsenate and chromate.

The following solvents were prepared:

A. *tert.*-Butyl alcohol, water and hydrochloric acid (sp. gr. 1.19) in the ratio 70:20:10,
B. *tert.*-Butyl alcohol, water and acetic acid (sp. gr. 1.055) in the ratio 70:20:10,
C. Solvent B with 1% (w/v) tartaric acid,
D. Solvent B with 1% (w/v) citric acid,
E. Solvent B with 1% (w/v) malonic acid.

RESULTS

The R_L and R_T values and the sequences of separation are given in the following tables. The square brackets indicate that the enclosed cations have a portion of their migration zone in common. Good results are achieved only with solvent A, with which mixtures of at least 6 cations or 3 anions are easily separated into distinct bands. With solvents B and C, only a separation of a ternary mixture is possible. Solvent D does not give any effective separation, whereas solvent E allows the separation of three anions. Because solvents A and E are more effective, R_L and R_T values of cations and anions with solvent A and those of anions with solvent E have been tabulated.

The presence of acetic acid as one of the components of a solvent contributes to the formation of diffuse bands and even with complexing agents, such as tartaric, citric or malonic acid, no improvement is observed; in some cases the complexing agents simply alter the rate of movement of the ions.

Although from the *R* values of the alkaline earths their separation appears to be possible, it was found that only magnesium can be separated from the mixture. Similarly only lithium can be separated from a mixture of the alkali metals.

TABLE I

R values ± 0.02. Temp. 35° ± 3°

Solvent A					
Ions	R_L	R_T	*Ions*	R_L	R_T
Li^+	0.68	0.40	Fe^{+3}	0.76	0.72
Na^+	0.32	0.19	Be^{+2}	0.60	0.51
K^+	0.29	0.21	Ti^{+4}	0.33	0.31
Rb^+	0.23	0.15	UO_2^{+2}	0.25	0.18
Cs^+	0.32	0.25	Cr^{+3}	0.24	0.16
			Al^{+3}	0.25	0.18
			Th^{+4}	0.12	0.07
Mg^{+2}	0.37	0.29			
Ca^{+2}	0.25	0.17	Ce^{+3}	0.13	0.07
Ba^{+2}	0.11	0.02	ZrO^{+2}	0.03	0.00
Sr^{+2}	0.16	0.07	Nb^{+5}	0.00	0.00
			Ta^{+5}	0.00	0.00
Zn^{+2}	1.00	0.96			
Mn^{+2}	0.42	0.36			
Co^{+2}	0.29	0.23			
Ni^{+2}	0.21	0.15			

Sequence of separation:

Zn–Mn–[Co–Ni]

Sequence of separation:

Fe–Be–Ti–(U or Cr or Al)–(Ce or Th)–(Zr or Nb or Ta)

TABLE II

R values ± 0.02. Temp. 35° ± 3°

Solvent A			*Solvent E*		
Ions	R_L	R_T	*Ions*	R_L	R_T
VO_3^-	0.41	0.28	VO_3^-	0.26	0.00
AsO_4^{-3}	0.94	0.91	AsO_4^{-3}	0.58	0.42
WO_4^{-2}	0.05	0.00	WO_4^{-2}	0.22	0.00
MoO_4^{-2}	0.30	0.23	MoO_4^{-2}	0.10	0.00
PO_4^{-3}	1.00	0.93	PO_4^{-3}	0.43	0.21
CrO_4^{-2}	0.40	0.35	CrO_4^{-2}	0.31	0.18

Sequence of separation:

PO_4^{-3}–VO_3^-–WO_4^{-2};
PO_4^{-3}–MoO_4^{-2}–WO_4^{-2};
AsO_4^{-3}–VO_3^-–WO_4^{-2};
and AsO_4^{-3}–MoO_4^{-2}–WO_4^{-2}

Sequence of separation:

AsO_4^{-3}–CrO_4^{-2}–MoO_4^{-2}

A comparison of the R values of the cations with the solvent *tert.*-butyl alcohol–water–hydrochloric acid with those of the mixture acetone–water–hydrochloric acid, shows that the movements of ferric, uranyl, molybdate and tungstate ions are slow in the former solvent, whereas the rates of movement of the other ions studied are more or less the same in both solvents.

SUMMARY

A study has been made of the separation of ions of the alkali metals, alkaline earth metals, elements of groups IIIA and B and of anions, such as arsenate, phosphate, vanadate, molybdate, tungstate and chromate, with solvent mixtures of *tert.*-butyl alcohol, water and hydrochloric or acetic acid in the ratio of 7:2:1, and with or without tartaric, citric or malonic acid. The solvent mixture with hydrochloric acid as one of the components was found to be most effective for the separation of six cations or three anions from their mixtures. The R_L and R_T values and the sequences of separations have been recorded.

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Received March 6th, 1958

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

II. BISMUTHIOL II AS AN ANALYTICAL REAGENT

by

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The reagent bismuthiol II, introduced by Dubsky *et al.*[1] and utilized by Majumdar[2] as a colorimetric reagent for bismuth, was shown[3,4] to be highly effective for the gravimetric determination of bismuth, palladium, platinum, lead, silver, thallium and copper.

While studying the nature of the complexes formed with this reagent, it was found that the red compound formed with palladium can be extracted like the complex with bismuthiol I, from an acid solution (0.1N–1N) by means of methyl isobutyl alcohol, methyl isopropyl alcohol, ethyl acetate, chloroform, ether, isopropyl ether, amyl alcohol, *n*-butyl alcohol and benzene, and that it is soluble in semipolar solvents, such as, acetone, methyl alcohol, dioxane and methyl cellosolve. The colour reaction is independent of pH and though the system does not show a sharp peak of maximum absorption, it obeys Beer's law at a palladium concentration of 0.4 μg–8.0 μg/ml measured at any wavelength between 410 mμ and 430 mμ. Below pH 3.0, the colour system is not very stable but above it, measured up to pH 10.0, the intensity of the colour remains the same, even for as long as about 24 h.

The cations of alkalis, alkaline earths, bismuth, antimony, tin, cadmium, lead, zinc, manganese, nickel, cobalt, titanium, zirconium, thorium, rare earths, aluminium, beryllium and anions of chloride, bromide, iodide, fluoride, sulphate, thiosulphate, nitrate, nitrite, phosphate, arsenate, arsenite, molybdate, tungstate, borate, oxalate, citrate, benzoate, salicylate, tartrate, acetate, formate and complexone III have no effect on the colour system.

The ions of platinum, gold, copper, chromium, iron, mercury, silver, thallium, uranium, vanadate and cyanide interfere.

Bismuthiol II is in many respects preferable to other well-known colorimetric reagents such as *p*-nitroso-diphenylamine, *p*-nitroso-diethylaniline and *p*-nitroso-dimethylaniline used by YOE *et al.*[5], since compared to them its colour reaction with palladium is instantaneous and highly sensitive; the sensitivity is either 0.06 μg of palladium per cm² (practical) or 0.01 μg and 0.012 μg of palladium per cm² at 410 mμ and 420 mμ respectively according to SANDELL's definition[6]. The system is stable for a long period over a large pH range and is unaffected even by the presence of a large number of ions and complexing agents.

Determined by JOB's method[7] of continuous variation, the composition of the complex in solution is $Pd(C_8H_5N_2S_3)_2$ and its dissociation constant is on the average $2.8 \cdot 10^{-12}$ at 25°.

EXPERIMENTAL

Apparatus and solutions

The apparatus and solutions were the same as those used in an earlier communication[8].

A 0.25% aqueous solution of the potassium salt of bismuthiol II of m.p. 248° was used as a colour-forming reagent.

Equimolecular and non-equimolecular solutions of palladium and of the reagent were prepared in order to study the composition and the dissociation constant of the complex by JOB's method.

Colour reaction

In an acid or alkaline medium, Bismuthiol II reacts instantaneously with palladium giving a red colour or a red precipitate, dependent on the concentration of palladium. The red compound is fairly soluble in semi-polar solvents, such as acetone, methyl alcohol, dioxane and methyl cellosolve, less soluble in ethyl alcohol and completely insoluble in non-polar solvents. Since the compound has a tendency to precipitate from the aqueous solution, samples containing only 4 μg of palladium per ml show within 30 min a 3% deviation in the values of the optical density. This deviation due to precipitation is however obviated if ethyl or methyl alcohol, acetone or methyl cellosolve at least to the extent of 10% (v/v) is added to the solution. Complexone III, which is used as a masking agent for ions, has no influence on the system, when not more than 100 mg of it are present in a volume of 25 ml.

In Fig. 1 the absorbance curves are recorded of (1) the palladium complex against the reagent solution, (2) the palladium complex against water and (3) the reagent solution against water. From the curves it is evident that the optical density of the reagent decreases sharply from 400 mμ and is almost negligible from 410 mμ onwards. The palladium complex has no sharp peak of maximum absorption, but the decrease in absorption is practically the same from 410–430 mμ and hence all measurements were made at 420 mμ, which is the mean value.

Effect of solvent

Since in aqueous solution the optical density shows a deviation, attempts were made to cancel this with organic solvents such as ethyl alcohol, acetone, dioxane, pyridine and methyl cellosolve. Pyridine and ethyl alcohol reduce the colour intensity, dioxane renders the solution turbid and only acetone and methyl cellosolve, even when present to the extent of 50% (v/v), do not affect the optical density at or above 420 mμ. With only 10% (v/v) of acetone or methyl cellosolve, measurements can even be made at 410 mμ. Owing to the volatility of acetone, methyl cellosolve is preferred; the colour system prepared in a solution containing only 10% (v/v) of methyl cellosolve is very stable. Higher amounts of the said solvent may, however, cause salts to precipitate. Thus in the subsequent preparation of the colour system, the solution, contained at least 10% (v/v) or 2.5 ml of methyl cellosolve in a total volume of 25 ml.

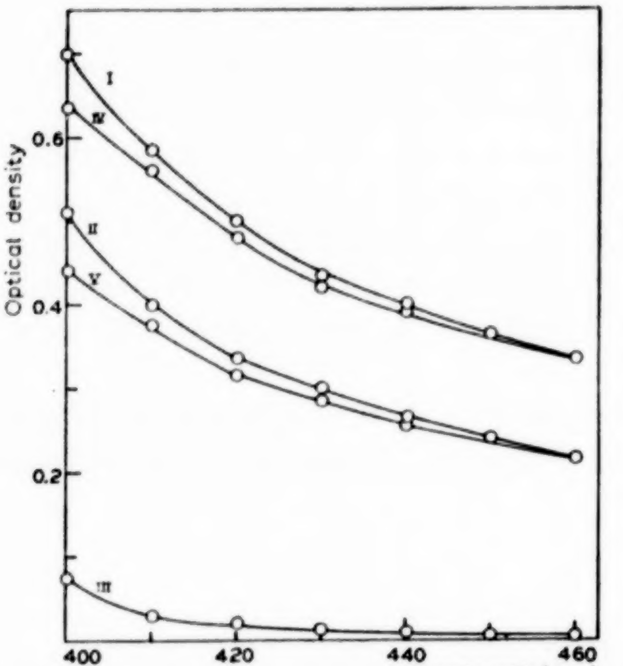

Fig. 1. Absorption regions of the colour system at pH 8.0. The system contains besides palladium, 4 ml reagent and 2.5 ml methyl cellosolve in a total volume of 25 ml. I. 6 μg Pd per ml; II 4 μg Pd per ml; III. Without Pd; IV. Corrected value (I—III); V. Corrected value (II—III).

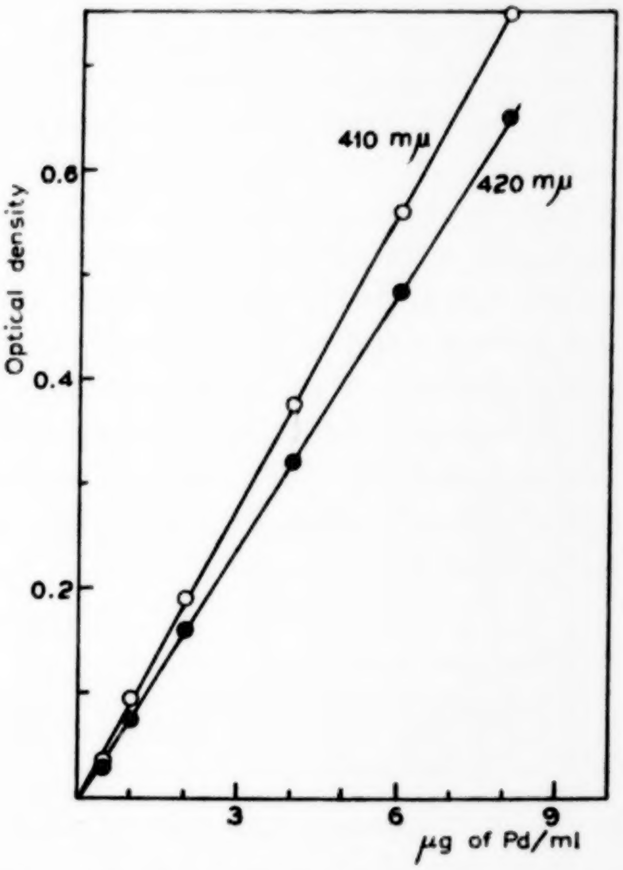

Fig. 2. Study of Beer's law. 4 ml reagent, 2.5 ml acetone or methyl cellosolve in a total volume of 25 ml pH 7.5.

Effect of reagent

The absorption at 420 or 430 mμ of a number of solutions, each containing 4 μg palladium per ml with different amounts of reagent (1 to 10 ml) and maintained at a pH of about 8.0, indicates that it is independent of the quantity of the reagent. For subsequent measurements, 4.0 ml of the reagent solution were added to the palladium solution and the volume was then made up to 25 ml.

Effect of pH, time and temperature

For the study of pH, dilute hydrochloric acid or ammonia was added to the palladium solution after the addition of the reagent and dilution to 25 ml as stated above. The optical density of every solution, adjusted to a definite pH, was measured against a reagent blank; the results obtained show that at a pH between 3 and 10, deviation is less than 1% even on standing for 24 h, while after 48 h, a 6% deviation is observed.

The colour system was also found to be stable at a temperature between 20 and 30°; at 35° it exhibited a deviation of about 1%.

Beer's law and sensitivity

That the colour system when measured against the reagent blank obeys Beer's law for concentrations ranging from 0.4 μg to 8.0 μg of palladium per ml is evident from the fact that straight lines passing through the origin are obtained when the optical densities at 410 mμ and 420 mμ are plotted against the respective concentrations, the optical density for 4 μg of palladium per ml being 0.374 and 0.317 at 410 mμ and 420 mμ respectively (*cf.* Fig. 2).

The sensitivity of the colour reaction is 0.067 μg palladium per cm^2 (practical); 0.01 μg and 0.012 μg palladium per cm^2 at 410 mμ and 420 mμ respectively[6].

Procedure

4 ml of the reagent solution are added to an aliquot quantity of a standard palladium solution. The pH of the solution is adjusted to any value between 3 and 10 with dilute hydrochloric acid or ammonia, and then 4 ml of the reagent solution, 2.5 ml of methyl cellosolve and a few ml of water to make up the volume to 25 ml are added successively. After thorough mixing, a portion of the solution is transferred to a 1-cm absorption cell and the optical density is measured. In the same way, a reagent blank solution without palladium is prepared and the optical density measured.

Effect of diverse ions

The interference of ions is studied by measuring the colour intensity produced on the addition of the solution of the ion under investigation to the solution of palladium (100 μg) in a 25-ml volumetric flask with 5 ml of the complexone III solution and 4 ml of the reagent solution. After the adjustment of the pH, 2.5 ml of methyl cellosolve and water to make up the volume to 25 ml are added, according to the procedure described above. The optical density of the resulting solution in a 1-cm cell is then measured at 420 mμ against the reagent blank. An ion is considered to interfere if the absorbance differs by more than 0.005 from the value obtained with palladium alone. The limits of tolerance of the diverse ions are summarized in Table I. Ions of platinum, gold, copper, chromium, iron, mercury, silver, thallium, uranium, vanadate and cyanide interfere.

Composition and dissociation constant of the palladium complex in solution

For the evaluation of the composition of the complex, the absorption of mixtures (keeping the total volume constant) of equimolecular solutions at 20–25° was measured at 420 mμ, at which wavelength small concentrations of the reagent show negligible absorption. The experimental data are represented graphically in Fig. 3, which was obtained by plotting the corrected and uncorrected optical densities against the composition of the mixtures; corrected values are obtained by measuring the colour system against a palladium solution which shows some absorption. Density measurements of the mixtures of equimolecular solutions lead definitely to the conclusion that the complex between palladium and the reagent is formed when the reactants are in the ratio of 1:2, which value agrees well with the composition of the

TABLE I

Ions	*Maximum amount of ion tolerated* μg	*Ion/Pd ratio at maximum tolerance limit*
Pb^{+2}	150	37.5
Cd^{+2}	100	25.0
Co^{+2}	50	12.5
Mn^{+2}	100	25.0
Ni^{+2}	50	12.5
Zn^{+2}	100	25.0
Ca^{+2}	200	50.0
Ba^{+2}	200	50.0
Sr^{+2}	200	50.0
Mg^{+2}	200	50.0
Be^{+2}	50	12.5
Ti^{+4}	50	12.5
Th^{+4}	150	37.5
Al^{+3}	100	25.0
Ru^{+3}	10	2.5
Os^{+4}	10	2.5
Ir^{+4}	20	5.0
Rh^{+3}	5	1.25
Bi^{+3}	100	25.0
Sn^{+4}	50	12.5
Zr^{+4}	100	25.0
Cl^-	250	62.5
F^-	150	37.5
Br^-	200	50.0
I^-	200	50.0
NO_3^-	250	62.5
NO_2^-	250	62.5
SO_4^{-2}	250	62.5
$S_2O_3^{-2}$	200	50.0
PO_4^{-3}	200	50.0
AsO_4^{-3}	250	62.5
AsO_3^{-3}	250	62.5
BO_3^{-3}	250	62.5
MoO_4^{-2}	200	50.0
WO_4^{-2}	200	50.0
Acetate	250	62.5
Formate	250	62.5
Oxalate	120	30.0
Benzoate	200	50.0
Salicylate	200	50.0
Citrate	250	62.5
Tartrate	250	62.5

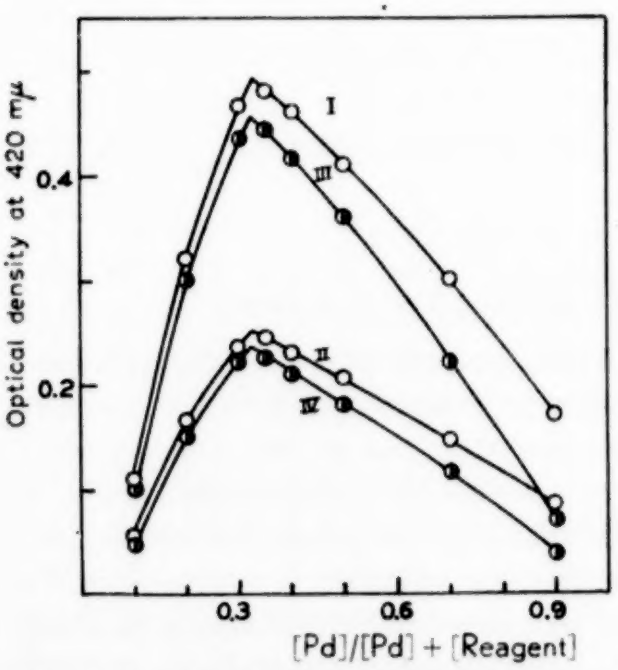

Fig. 3. Mixtures of equimolecular solutions. I. $1.88 \cdot 10^{-4}M$; II. $0.94 \cdot 10^{-4}M$; III. and IV. Corrected values.

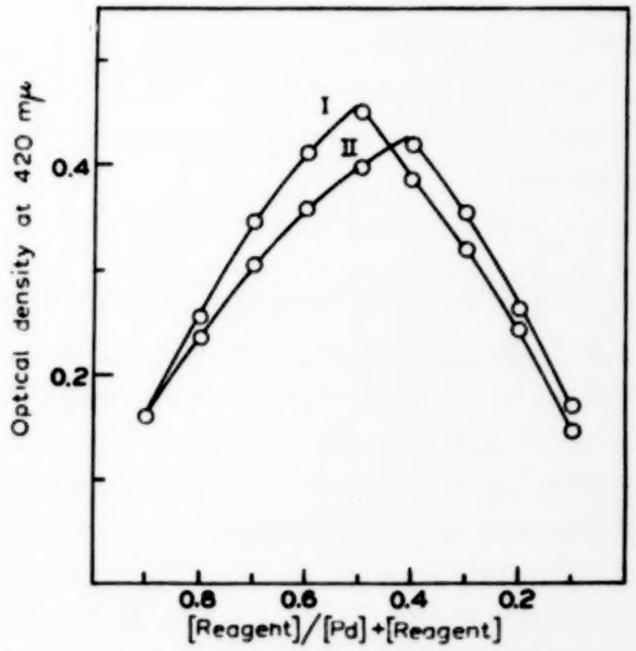

Fig. 4. Mixtures of non-equimolecular solutions. I. $0.94 \cdot 10^{-4}M$ Pd and $1.88 \cdot 10^{-4}M$ reagent; II. $0.94 \cdot 10^{-4}M$ Pd and $2.82 \cdot 10^{-4}M$ reagent.

compound isolated from solution. The actual value as obtained from the figure is 1:2.07. This somewhat high value of the reagent is mainly due to its slight decomposition.

From the absorption data (Fig. 4) of the mixtures of non-equimolecular solutions, the dissociation constant K has been calculated in the same way as stated in a previous paper[8]. The values of m and n being 1 and 2 respectively, the values of x, p, c and K are as given below:

Curve	*Conc. of Pd M*	*Conc. of bismuthiol II M*	x	p	K
I	$0.94 \cdot 10^{-4}$	$1.88 \cdot 10^{-4}$	0.508	2	$3.8 \cdot 10^{-12}$
II	$0.94 \cdot 10^{-4}$	$2.82 \cdot 10^{-4}$	0.412	3	$1.8 \cdot 10^{-12}$

K (mean) $= 2.8 \cdot 10^{-12}$

SUMMARY

A method for the spectrophotometric determination of palladium with bismuthiol II is described. The colour reaction is instantaneous and at 20–30° the system is stable for about 24 hours when maintained at a pH between 3 and 10. The colour system shows no sharp peak of maximum absorption but measurements can be made at any wavelength between 410 mμ and 430 mμ, preferably at 420 mμ. In this region the system obeys Beer's law at a palladium concentration of 0.4 μg to 8.0 μg per ml. The sensitivity of the reaction is 0.06 μg palladium per cm² (practical) or 0.01 μg and 0.012 μg of palladium per cm² at 410 mμ and 420 mμ respectively (SANDELL). Acetone and methyl cellosolve stabilize the system. Excess of reagent and a large number of cations and anions are completely without effect. The composition of the complex in solution, which agrees well with that of the isolated compound, is $Pd(C_8H_5N_2S_3)_2$ with an average dissociation constant of $2.8 \cdot 10^{-12}$ at 25°.

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Received March 13th, 1958

THE SEPARATION OF INORGANIC ISOMERIC *CIS-TRANS* COMPOUNDS BY PAPER CHROMATOGRAPHY AND THE EFFECT OF CONFIGURATION ON R_F VALUES

by

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In a study of the application of paper chromatography to the separation of stereoisomeric inorganic compounds, we established, as early as 1954, that in this way inorganic isomeric *cis–trans* compounds can be resolved into the components[1].

In the same year, YAMAMOTO, NAKAHARA AND TSUCHIDA[2] published a paper in which the alteration of the R_F values with the number of nitro groups in the complex cobalt ammines was investigated. In this study they determined the R_F values of *cis* and *trans* $[Co(NH_3)_4(NO_2)_2]Cl$, but gave no indication of attempts to separate the *cis* and *trans* forms.

Following the initial investigations, we have so far separated 12 pairs of isomeric compounds belonging to the group of electrolytes with complex cations, *i.e.**:

1. $[Co\ en_2(NO_2)_2]NO_3$
2. $[Co\ en_2(NO_2)_2]I$
3. $[Co\ en_2Cl_2]Cl$
4. $[Co(NH_3)_4(NO_2)_2]NO_3$
5. $[Co(NH_3)_4(NO_2)_2]I$
6. $[Co\ en_2Br_2]Br$
7. $[Co\ en_2(NCS)_2]Cl$
8. $[Cr\ en_2(SCN)_2]SCN$
9. $[Co\ en_2(NO_2)Cl]Cl$
10. $[Co\ en_2(NCS)Cl]Cl$
11. $[Co\ en_2(NH_3)Cl]Cl_2$
12. $[Pt(NH_3)_2Py_2]Cl_2$

Our experiments have confirmed that it is possible to separate *cis–trans* isomers by paper chromatography if acetone be used as the chief component of the solvent mixture for development. In addition to acetone, the mixture should contain water, mineral acid or potassium iodide. By combining these reagents we have prepared seven basic solvent mixtures, by means of which the separation of *cis–trans* isomers has been achieved in 11 out of a total of 12 complex compounds studied. Only in the case of $[Cr\ en_2(SCN)_2]SCN$ the separation could not be achieved with a solvent mixture containing acetone. In that case, therefore, a mixture of ether, ethanol and water was used.

The ratio of the components in the above-mentioned solvent-systems is as follows:

1. 70 ml acetone + 20 ml water + 10 ml HCl (sp.gr. 1.19).
2. 80 ml acetone + 15 ml water + 5 ml HCl (sp.gr. 1.19).
3. 85 ml acetone + 7.5 ml water + 7.5 ml HCl (sp.gr. 1.19).

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* These compounds were selected because of their relative stability and because they have been well studied. The separation of the *cis* and *trans* isomers of the first three compounds has already been described in our first paper[1].

References p. 492

4. 95 ml acetone + 5 ml HCl (sp.gr. 1.19).
5. 65 ml acetone + 30 ml water + 5 ml HNO_3 (sp.gr. 1.42).
6. 75 ml acetone + 5 ml water + 20 ml HBr (sp.gr. 1.38).
7. 85 ml acetone + 15 ml water + 1 g solid KJ.
8. 90 ml ether + 15 ml absolute ethanol + 5 ml water.

EXPERIMENTAL

All the isomeric compounds investigated in this paper were prepared by methods already known; their composition was checked by gravimetric analysis (Table I). Cobalt was determined as $CoSO_4$, chromium as Cr_2O_3, and platinum as Pt.

All the separations described were made on Whatman No. 1 paper, by ascending chromatography. The temperature during the separations was 20–22°.

Chromatography was always carried out with completely fresh solutions of the isomers in water; in the case of more soluble salts, the concentration of the solutions ranged from 0.05 to 0.1 *M* with respect to each component, while for the less soluble salts a saturated solution at a temperature of about 50° was used. By means of a micropipette, about $3 \cdot 10^{-3}$ ml of solution was placed on each strip as a narrow line.

TABLE I

No.	*Compound*	*Preparation (Reference)*	*Found %*		*Calculated %*
			cis	*trans*	
1.	$[Co(NH_3)_4(NO_2)_2]NO_3$	3,4	Co: 21.04	21.09	20.97
2.	$[Co(NH_3)_4(NO_2)_2]I$	5	Co: 17.14	16.87	17.03
3.	$[Co\ en_2Br_2]Br$	6,7	Co: 13.86	14.01	14.07
4.	$[Co\ en_2(NCS)_2]Cl$	8	Co: 17.77	17.66	17.82
5.	$[Cr\ en_2(SCN)_2]SCN$	9,10	Cr: 15.18	15.15	15.01
6.	$[Co\ en_2(NO_2)Cl]Cl$	7	Co: 19.76	19.87	19.91
7.	$[Co\ en_2(NCS)Cl]Cl$	7,8	Co: 18.90	19.00	19.13
8.	$[Co\ en_2(NH_3)Cl]Cl_2$	7	Co: 19.52	19.35	19.48
9.	$[Pt(NH_3)_2Py_2]Cl_2$	11,12	Pt: 42.51	42.26	42.50

Complex cobalt compounds were detected by immersing dried strips in a 2*N* solution of ammonium sulphide; $[Cr\ en_2(SCN)_2]SCN$ was detected by immersing dried strips in a 2*N* solution of ferric chloride, while $[Pt(NH_3)_2Py_2]Cl_2$ was detected by immersing dried strips in a 4*N* solution of sodium formate and heating to 120°.

The R_F values obtained and other experimental data are given in Table II.

RESULTS

From Table II and the photographs of the chromatograms obtained (Fig. 1), it can be seen that the R_F values in all the cases investigated are considerably higher for the *cis* form than the R_F values for the *trans* form. This regularity is even more clearly illustrated by Fig. 2. From Table II it can also be seen that the R_F values have no connection with the solubility of isomeric pairs, as the regularity in the R_F values exists regardless of whether one isomer is more or less soluble than the other.

In short, it can be concluded that of the isomeric compounds belonging to the group of electrolytes with complex cations, the *cis* isomers have higher R_F values than the *trans* forms, when a solvent mixture with acetone as chief component is used for chromatographic development.

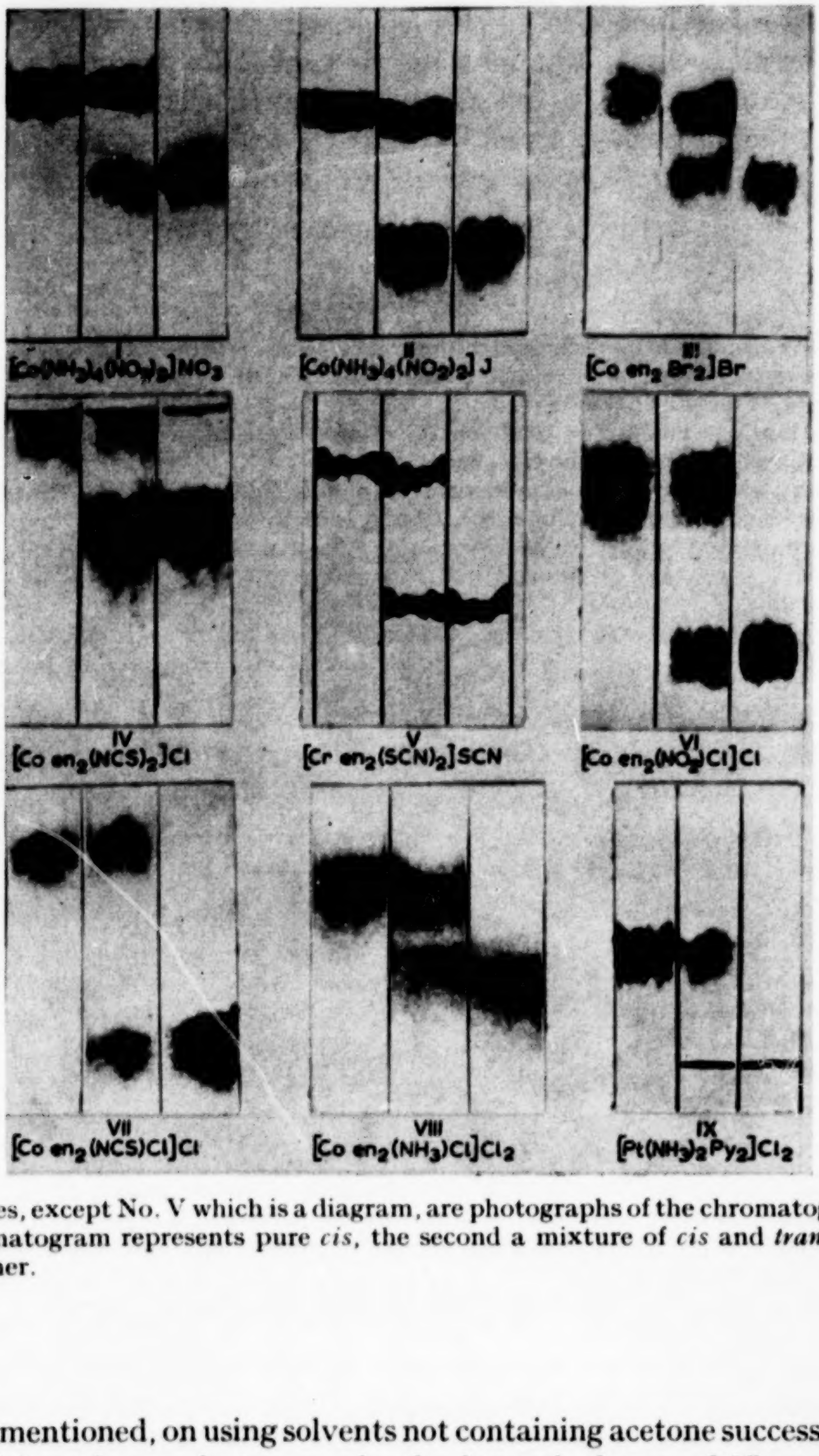
I
$[Co(NH_3)_4(NO_2)_2]NO_3$
II
$[Co(NH_3)_4(NO_2)_2]$ J
III
$[Co\ en_2 Br_2]Br$
IV
$[Co\ en_2(NCS)_2]Cl$
V
$[Cr\ en_2(SCN)_2]SCN$
VI
$[Co\ en_2(NO_2)Cl]Cl$
VII
$[Co\ en_2(NCS)Cl]Cl$
VIII
$[Co\ en_2(NH_3)Cl]Cl_2$
IX
$[Pt(NH_3)_2Py_2]Cl_2$

Fig. 1. All figures, except No. V which is a diagram, are photographs of the chromatograms obtained. The first chromatogram represents pure *cis*, the second a mixture of *cis* and *trans* and the third pure *trans* isomer.

As already mentioned, on using solvents not containing acetone successful separation was achieved in only one instance, *viz.* the isomeric forms of $[Cr\ en_2(SCN)_2]SCN$. It is therefore not yet possible to say whether this regularity is of broader significance, *i.e.* whether the *cis* forms have higher R_F values than the *trans* forms, regardless of the composition of the solvent mixture used.

If it were confirmed in the case of other complex compounds, this regularity, which might be due to the structure of cellulose besides other factors, could be applied to the determination of configuration.

The proposed method is simpler than the other chemical and physical methods for the determination of configuration, and it also has the advantage that only small quantities of the isomers to be investigated are required.

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TABLE II

No.	Compound	Solvent mixture No.	Time of development in h	R_F values cis	R_F values trans	Solubility in moles/l water* cis	Solubility in moles/l water* trans
1.	$[Co(NH_3)_4(NO_2)_2]NO_3$	5	3	0.73	0.46	about 0.132 (23°)	about 0.013 (20°)
2.	$[Co(NH_3)_4(NO_2)_2]I$	7	3	0.85	0.62	0.0900 (23°)	0.0198 (18°)
3.	$[Co\,en_2(NO_2)_2]NO_3$	5	22	0.73	0.62	0.0362 (18°)	0.0663 (16.5°)
4.	$[Co\,en_2(NO_2)_2]I$	7	22	0.66	0.45	0.0141 (22°)	0.0668 (16.5°)
5.	$[Co\,en_2Cl_2]Cl$	1	24	0.52	0.42	0.13	over 0.88
6.	$[Co\,en_2Br_2]Br$	6	6	0.74	0.56	Sparingly soluble	about 0.096
7.	$[Co\,en_2(NCS)_2]Cl$	4	3	0.97	0.74	0.0159 (25°)	More soluble than *cis* isomer
8.	$[Cr\,en_2(SCN)_2]SCN$	8	20	0.79	0.60	about 0.0196 (20°)	about 0.0303 (20°)
9.	$[Co\,en_2(NO_2)Cl]Cl$	3	4	0.63	0.17	0.169 (12°)	—
10.	$[Co\,en_2(NCS)Cl]Cl$	1	16	0.87	0.64	*Cis* isomer is less soluble	
11.	$[Co\,en_2(NH_3)Cl]Cl_2$	1	48	0.57	0.50	—	—
12.	$[Pt(NH_3)_2Py_2]Cl_2$	2	2	0.41	0.00	—	0.185 (18°)

* The values for solubility are taken from GMELIN's *Handbuch der anorganischen Chemie* (Kobalt, Teil B (1930); Band V Abt. 3 (1915) and Band III Abt. 1 (1912); most of them have been recalculated in order to express solubility in gram-moles per liter of water.

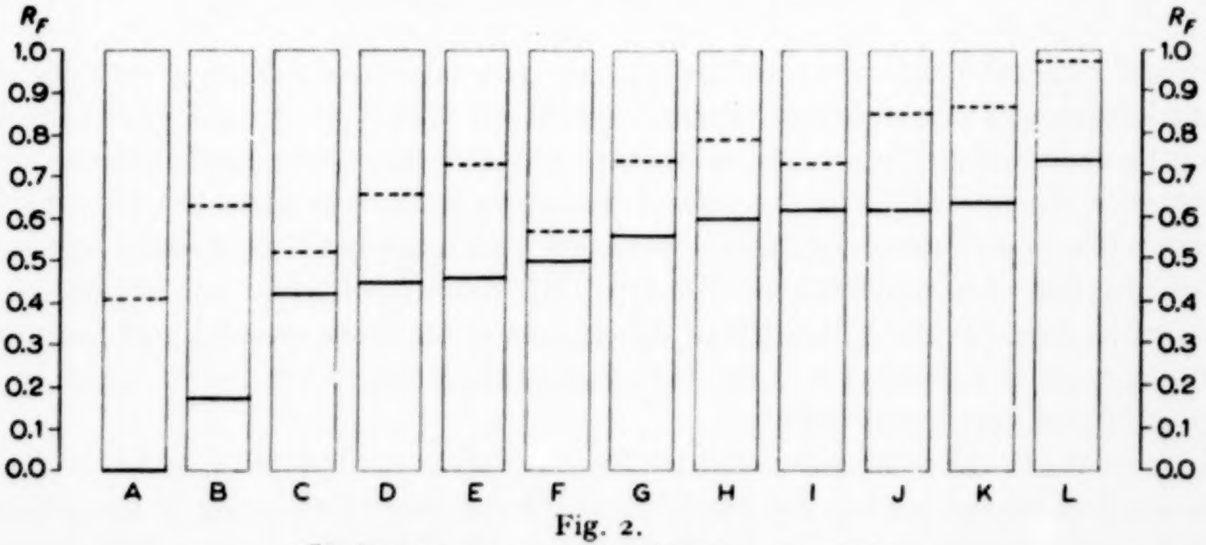

Fig. 2.

Cis isomer – – – –; *trans* isomer ————.

A. $[Pt(NH_3)_2Py_2]Cl_2$
B. $[Co\,en_2(NO_2)Cl]Cl$
C. $[Co\,en_2Cl_2]Cl$
D. $[Co\,en_2(NO_2)_2]I$
E. $[Co(NH_3)_4(NO_2)_2]NO_3$
F. $[Co\,en_2(NH_3)Cl]Cl_2$
G. $[Co\,en_2Br_2]Br$
H. $[Cr\,en_2(SCN)_2]SCN$
I. $[Co\,en_2(NO_2)_2]NO_3$
J. $[Co(NH_3)_4(NO_2)_2]I$
K. $[Co\,en_2(NCS)Cl]Cl$
L. $[Co\,en_2(NCS)_2]Cl$

For clarity, the chromatograms are arranged in the order of increasing R_F values for *trans* isomers.

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SUMMARY

It has been established that of all the inorganic isomeric *cis–trans* compounds that have been separated by paper chromatography up to the present, the *cis* isomers have higher R_F values than the *trans* forms. On the basis of this regularity, a new method has been suggested for the determination of the configuration of inorganic isomeric *cis–trans* compounds.

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Received March 3rd, 1958

A SYSTEMATIC STUDY OF INSOLUBLE SUBSTANCES. I

by

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Several papers[1,2] have been published from this laboratory dealing with the systematic detection of insoluble substances in qualitative analysis. A number of substances which become difficultly soluble on heating was reported and included in the scheme of detection. In view of the marked effect of heating on the solubility of some substances a systematic investigation of those substances which are likely to become less soluble on heating has been undertaken. The result of this investigation has shown that the effect of heating on the solubility of substances is far more general and pronounced than is generally supposed and the list of substances which are called 'insoluble' has to be enlarged very considerably.

Because the problem was investigated from the analytical point of view, the approximate method for measuring the insolubility of substances was based on the procedure used in separating the insoluble residue from the soluble portion in qualitative analysis. This enabled us not only to gain some idea as to how these substances would behave in analysis, but also to compare their behaviour with those substances which have already been included in the list of insoluble substances. The standard procedure which has been recommended in the more comprehensive scheme[1] of qualitative analysis for

TABLE I

Name of the compound	*2 h ignition at 900°*		*9 h additional ignition at 900°*		*0.01 g of the substance in 1 standard acid treatment*	*Formula given in literature*	*Formula found*
	Percentage left undissolved in 1 standard acid treatment	*Percentage left undissolved in 5 standard acid treatments*	*Percentage left undissolved in 1 standard acid treatment*	*Percentage left undissolved in 5 standard acid treatments*			
Chromites							
1. Magnesium chromite	91.0	80.4	99.1	98.8	Does not dissolve completely	$Mg(CrO_2)_2$	$Mg(CrO_2)_2$
2. Zinc chromite	99.0	98.2	—	—	,,	$Zn(CrO_2)_2$	$Zn(CrO_2)_2$
3. Cadmium chromite	99.5	99.0	—	—	,,	$Cd(CrO_2)_2$	$Cd(CrO_2)_2$
4. Manganese chromite	97.5	90.6	99.0	99.0	,,	$Mn(CrO_2)_2$	$Mn(CrO_2)_2$
5. Cobalt chromite	97.0	89.3	99.6	99.3	,,	$Co(CrO_2)_2$	$CoO.Co(CrO_2)_2$
6. Copper chromite	99.5	99.0	—	—	,,	$Cu(CrO_2)_2$	$2\,CuO.3Cu(CrO_2)_2$
7. Nickel chromite	98.0	95.3	98.0	96.4	,,	$Ni(CrO_2)_2$	$Ni(CrO_2)_2$
8. Beryllium chromite	99.5	99.4	—	—	,,	$Be(CrO_2)_2$	$Be(CrO_2)_2$
9. Cerium chromite	97.0	90.0	99.0	96.8	,,	$CeO_2.2Cr_2O_3$	$CeO_2.2.5Cr_2O_3$
10. Uranium chromite	96.0	80.0	96.0	94.8	,,		$UO_3.2Cr_2O_3$
11. Zirconyl chromite	99.8	99.6	—	—	,,		$ZrO(CrO_2)_2$
Aluminates							
1. Copper aluminate	96.0	76.3	96.0	86.8	Does not dissolve completely	$Cu(AlO_2)$	$Cu(AlO_2)_2$
2. Cobalt aluminate	96.0	93.8	99.6	97.2	,,	$Co(AlO_2)_2$	$Co_2O_3.Al_2O_3$
3. Zinc aluminate	99.2	98.8	—	—	,,	$Zn(AlO_2)_2$	$Zn(AlO_2)_2$
4. Manganese aluminate	97.0	95.3	99.0	97.2	,,	$Mn(AlO_2)_2$	$Mn(AlO_2)_3$
5. Nickel aluminate	88.0	71.0	88.0	71.0	,,	$Ni(AlO_2)_2$	$Ni(AlO_2)_2$
Phosphate							
1. Chromium phosphate	95.0	94.8	100	100	Does not dissolve completely	$CrPO_4$	$CrPO_4$
Arsenates (heated at 800°)							
1. Zirconium pyroarsenate	97.4	87.0	99.5	99.0	Does not dissolve completely	$ZrAs_2O_7$	$ZrAs_2O_7$
2. Zirconyl pyroarsenate	97.2	92.0	99.5	99.0	,,	$Zr_2As_2O_9$	$Zr_2As_2O_9$
3. Titanyl pyroarsenate	98.0	97.0	98.1	97.3	,,	$Ti_2As_2O_9$	$Ti_2As_2O_9$
4. Chromium pyroarsenate	99.8	99.6	—	—	,,	$Cr_4(As_2O_7)_3$	$Cr_4(As_2O_7)_3$

separating the insoluble portion is to evaporate slowly to dryness 0.5 g of the mixture with 15 ml of conc. HNO_3, followed by 15 ml of conc. HCl when about 5 ml of the conc. HNO_3 is left. This was the uniform method adopted in the present investigation. After the weighed portion of the substance had been subjected to this treatment, it was treated with dil. HCl, filtered, washed and weighed again to find out what percentage remained undissolved.

Although the treatment outlined above gave a fairly good idea of the insolubility of the substances, it was still thought necessary to apply more rigorous tests to find out whether they had become sufficiently insoluble to be included in the list of insoluble substances. This was done in two ways (1) by subjecting each substance to the above mentioned acid treatment five times in succession, (2) by taking a very small quantity of the substance (0.01 g) and subjecting it to the standard acid treatment to see whether it was appreciably affected. Only those substances which could stand all these tests and were found insoluble to the extent of at least 80% were included in the list. The two exceptions are nickel ferricyanide and heated nickel aluminate whose insolubility was found to be less than 80%.

With the exception of the insoluble manganic metaphosphate, ferricyanides and nitroprussides which cannot be heated, all other insoluble substances were prepared by heating the corresponding compounds in a muffle furnace at a temperature of 900° for 2 h. Only in the case of arsenates was the temperature kept at 800° to avoid any decomposition. As will be seen from the tables, heating for 2 h rendered most of the substances insoluble to the extent of over 90% in one standard acid treatment. Successive treatments with acids did not further dissolve the substance to a considerable extent, though in a few cases with five treatments only 70–80% of the substance was left undissolved.

Those substances which had not become insoluble to the extent of at least 99% on heating for 2 h, were subjected to further heating in the muffle furnace at a temperature of 800°–900° for an additional period of 9 h. This further heating was found to increase the insolubility still more. In most cases the insolubility increased to 99% in one acid treatment and the resistance to successive treatments also increased simultaneously. In a few cases, however, the insolubility was practically unaffected by this further heating.

With regard to the method of preparing the compounds which resist the solvent action of concentrated hydrochloric and nitric acids, the usual methods were followed in the case of nitroprussides, ferricyanides, arsenates and phosphates. Zirconium forms two arsenates with disodium hydrogen arsenate according to whether the nitrate or oxychloride is used. Both the arsenates are difficultly soluble in concentrated acids and quite insoluble after ignition. In the case of aluminates and chromites, the compound was prepared by adding an aqueous solution containing the sulphate or chloride of the metal to the slightly alkaline solution containing the freshly prepared sodium aluminate or chromite. The precipitate so obtained contains the aluminate or chromite together with the hydroxide of the metal. Several workers have reported the preparation of these aluminates[3] and chromites[4] by heating a mixture of the oxides to a high temperature with or without a flux or by coprecipitation of the hydroxides of the metals from a solution, containing the two metallic ions, but the uniform method given above was found to be the most convenient and reliable and was followed in the case of all such compounds. Of course, before the heated aluminates and chromites were subjected

TABLE II

Name of the compound	*Percentage left undissolved in*		*0.01 g of the substance in 1 standard acid treatment*
	1 standard acid treatment	*5 standard acid treatments*	
	Phosphate		
1. Manganic metaphosphate	85.0	67.0	Does not dissolve completely
	Ferricyanides		
1. Cobalt ferricyanide	98.0	97.0	Does not dissolve completely
2. Nickel ferricyanide	85.0	57.0	
	Nitroprussides		
1. Nickel nitroprusside	99.0	98.0	Does not dissolve completely
2. Cobalt nitroprusside	97.0	96.0	
3. Copper nitroprusside	100	100	

to the standard acid treatment the excess of the metallic oxide was extracted by means of dilute hydrochloric acid.

In the case of compounds prepared by previous workers, the behaviour towards acids has been hinted at in a few cases, but these statements are of such a vague and general nature as to be of little use for practical purposes. A more definite and systematic study of the behaviour towards acids was, therefore, quite necessary.

The ignited compounds were also analysed to determine their composition. The compound was fused with caustic soda, potassium nitrate being added when chromium was present in the compound. The two metals were estimated by the usual methods and the percentage in the compound was calculated and compared with that of the compound already reported. The percentage was found to be the same as reported except in the case of the chromites of cobalt, copper and uranium and the aluminates of manganese and cobalt as will be seen from the tables.

Further work on other compounds which show a tendency to become difficultly soluble on heating is being carried out.

SUMMARY

A systematic study of substances, found by the authors to be insoluble, has been undertaken. It was found that the following substances were sufficiently resistant to the standard acid treatment to be considered insoluble: (a) Nitroprussides of Ni, Co and Cu. (b) Ferricyanides of Ni and Co. (c) Ignited chromites of Mg, Zn, Cd, Mn, Co, Cu, Ni, Be, Ce, U and Zr. (d) Ignited aluminates of Cu, Co, Zn, Mn and Ni. (e) Ignited arsenates of Zr, Ti and Cr. (f) Ignited phosphate of Cr and freshly prepared manganic metaphosphate. It has been found that in the large majority of cases the insolubility increases with the period of heating.

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Received February 28th, 1958

SPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM IN ALUMINIUM ALLOYS

by

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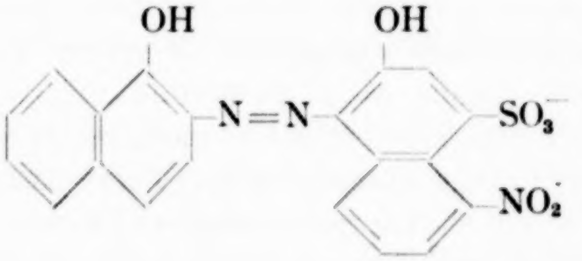
INTRODUCTION

Colorimetric methods for the determination of magnesium may be classified in two groups: those employing lake-forming reagents, such as Titan Yellow[1], Magneson[2] etc., and those in which soluble complexes of Mg are formed[3,4]. The high pH necessary for the formation of the magnesium lakes, the fading of the colours obtained and the serious interference of many ions (*e.g.* ammonium ion in the Titan Yellow method) make the lake-forming methods less desirable than those utilizing the formation of soluble coloured complexes.

The complexes of magnesium with Eriochrome Black T



have been the subject of a considerable number of recent investigations. SCHWARZENBACH AND BIEDERMANN[5] studied the behaviour of the reagent at different pH values and determined its equilibrium constants. HARVEY, KOMARMY AND WYATT[6] determined magnesium after its separation from calcium. YOUNG, SWEET AND BAKER[7] evolved a method for the simultaneous determination of magnesium and calcium at different pH values. YOUNG AND SWEET[8] also determined the proportions of magnesium and reagent in the complex by the method of continuous variations. Magnesium was determined spectrophotometrically with Eriochrome Black T by POHL[9-12], who applied the method to the determination of magnesium in various alloys; interfering elements were eliminated by means of oxine and the excess oxine was extracted before the determination of magnesium.

It was felt that a different approach to the problem of separating magnesium from the other constituents of the alloy and the introduction of a differential method for measuring the absorbance of the magnesium - Eriochrome Black T complex might lead to the development of a simple and reliable method for the determination of magnesium in aluminium alloys.

PRINCIPLE OF THE METHOD

Eriochrome Black T forms a wine-red complex with Mg^{+2} ions, which may be determined spectrophotometrically at pH 10.1 approximately[6]. Owing to the intense colour of the reagent, absorbance measurements must be made by a differential method.

For the determination of magnesium in an aluminium alloy, a preliminary separation of magnesium from the other constituents is necessary. The alloy is dissolved in sodium hydroxide, the hydroxide precipitate filtered off and redissolved with hydrochloric acid; after removal of interfering ions by an ammonium hydroxide-thioacetamide precipitation[13], magnesium is determined in an aliquot of the filtered solution.

APPARATUS AND REAGENTS

1. *A Unicam SP. 500 Spectrophotometer* was used for all absorbance measurements, with 0.5-cm matched Corex cells.
2. *Magnesium sulphate stock solution*. Dissolve 1.036 g $MgSO_4 \cdot 7H_2O$ in water containing 25 ml 2*N* H_2SO_4 and make up to 1 l. This solution contains 0.100 mg Mg^{+2} per ml. (This was confirmed by analysing the solution for Mg^{+2} by the pyrophosphate method[14]).
3. *Magnesium sulphate standard solution*. Reagent No. 2, diluted 50 times.
4. *Buffer solution*. Add 58 ml conc. NH_4OH to 7.5 g NH_4Cl and make up to 1 l with water.
5. *Potassium cyanide solution* (20 γ/ml).
6. *Eriochrome Black T solution*. Dissolve 120 mg of the reagent in small portions of methanol, heating gently and decanting* each portion into a 100-ml volumetric flask. Make up to mark with methanol.
7. *Sodium hydroxide*, pellets.
8. *Hydrochloric acid* (1 : 1).
9. *Methyl red indicator solution* (0.1%).
10. *Ammonium hydroxide*, conc.
11. *Thioacetamide solution*, 5%, freshly prepared.
12. *Wash solution "a"*, sodium hydroxide, 5%.
13. *Wash solution "b"*, 1% solution of ammonium chloride neutralized with ammonium hydroxide to the yellow colour of methyl red.

All reagents employed were AnalaR grade; bi-distilled water was used throughout.

PROCEDURE

A. Separation of magnesium from the other constituents of the alloy.

Weigh 100 mg of the alloy, containing 1 to 10%** magnesium, into a 150-ml Pyrex beaker and dissolve by the addition of 3 g sodium hydroxide and 20 ml water. As soon as the reaction slows down, place the beaker on a medium hot plate to effect complete solution of the alloy. Heat the solution to boiling, dilute to about 100 ml, allow the precipitate to settle and filter through a Whatman No. 1 filter paper. Wash the precipitate 3 times with hot wash solution "a" and later 3 times with hot water. Dissolve the washed precipitate in about 20 ml of hydrochloric acid (1 : 1) and collect the filtrate in the original beaker. Wash the filter paper thoroughly with hot water. Add one drop of methyl red indicator solution and neutralize with conc. ammonium hydroxide to the yellow colour of the indicator. Add 5 ml of 5% thioacetamide solution, dilute to about 100 ml, heat to boiling and allow the mixture to digest for 5 min on a warm plate. Filter through a Whatman No. 1 filter paper into a 1-l volumetric flask and wash the filter thoroughly with wash solution "b". Make the solution up to volume with bi-distilled water and take an appropriate aliquot for the colorimetric determination.

B. Preparation of a blank solution

For the preparation of a blank solution follow all the steps outlined in section A, except for the introduction of the alloy.

---

* Merck's Eriochrome Black T was employed; a small insoluble residue remains after decantation.

** Alloys containing 0.5 to 1% magnesium may be analysed by this method, provided a larger sample is taken (200 mg); for alloys containing less than 2% magnesium, the use of a collector for the hydroxide precipitate is advisable; a few mg of ferric sulphate are introduced into the hot hydroxide solution.

C. Determination of magnesium

Introduce an aliquot of the Mg^{+2} solution, containing 20γ to 70γ Mg^{+2}, into a 100-ml volumetric flask, add 25 ml buffer solution (reagent No. 4) and 10 ml* potassium cyanide solution (reagent No. 5) and dilute the solution to about 85 ml with water. Place the flask on a magnetic stirring plate and introduce a micro stirring-bar into it. Add 10 ml Eriochrome Black T solution (reagent No. 6); this must be done gradually, with constant stirring, from a burette. Make up to volume with water and continue stirring for 5 min.

Treat the blank solution in the same way, but add 8 ml Eriochrome Black T solution in place of the 10 ml used for the sample solution.

Introduce the blank solution into a 0.5-cm Corex cell and determine its absorbance at 520 mμ against distilled water in a matched cell. Find the exact wavelength (in the range 690 mμ to 710 mμ) at which the absorbance of the blank is identical with that measured at 520 mμ. Replace the distilled water by the blank solution and place the sample solution in the second cell. Measure the absorbance at 520 mμ and at the wavelength determined as described above. The difference between the two values obtained gives the amount of magnesium present in the sample solution, as determined from the calibration curve. Calculate the magnesium content of the sample by multiplying this result by the appropriate dilution factor (see example below).

D. Construction of the calibration curve

Treat appropriate aliquots of magnesium sulphate standard solution (reagent No. 3) as described in section C and in each case determine the absorbance of the coloured solution obtained. Repeat the determination 5 to 10 times for each Mg^{+2} content and take an average value for the construction of the calibration curve.

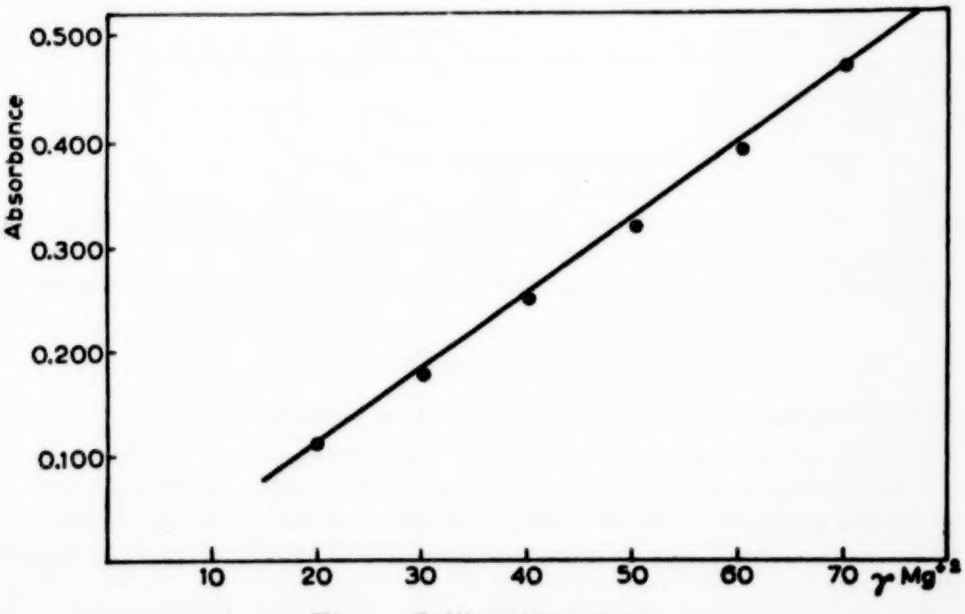


Fig. 1. Calibration curve.

E. Calculation of results, practical example

97.81 mg of an aluminium alloy were dissolved and treated as above. The sample solution-was made up to 1 l and a 25-ml aliquot was measured, for the development of the colour, into a 100-ml volumetric flask. The absorbances measured were:

520 mμ	702 mμ	difference
0.401	0.207	0.194

From the calibration curve (Fig. 1) this was found to correspond to 30.8γ Mg^{+2}. The magnesium content of the alloy is, therefore:

$$\% \text{ Mg} = \frac{30.8 \times 40 \times 100}{97.81 \times 1000} = 1.26\%$$

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* The volume of potassium cyanide must be measured accurately, to ensure equal cyanide content of both the sample and the blank solution; this is conveniently done by adding the potassium cyanide solution from a burette.

DISCUSSION

1. This method has been developed for the determination of magnesium in alloys containing 0.5 to 10% of magnesium; in alloys containing more than 2% magnesium, the precipitation of magnesium hydroxide during the dissolution of the alloy in sodium hydroxide will be quantitative and independent of the presence or absence of other constituents in the alloy. Whenever the magnesium content of the alloy falls below 2% and the alloy contains only small amounts of other elements whose hydroxides are insoluble in sodium hydroxide (*e.g.* Cu, Fe), the entire precipitate will be very small and may not always be quantitative. To prevent low results, it is advisable to introduce a few mg of ferric sulphate into the hot hydroxide solution; the ferric hydroxide formed acts as collector and does not affect the final determination of magnesium, as all the iron ions are removed in the thioacetamide precipitation step.

2. The thioacetamide precipitation also removes interfering ions such as Mn^{+2}, Cu^{+2}, Ni^{+2}, and Al^{+3} adsorbed by the hydroxide precipitate. Acting as a homogeneous precipitation reagent, thioacetamide causes the formation of an easily filterable precipitate, which also does not appreciably adsorb Mg^{+2} ions. Compared with the classic methods of separation, this procedure is less time-consuming.

3. A complete removal of interfering ions is necessary before the photometric determination of magnesium with Eriochrome Black T. Spot tests carried out after the thioacetamide precipitation showed faint traces of Cu^{+2} ions still present in the filtrate. The addition of a small amount of potassium cyanide was found to eliminate this interference. Potassium cyanide, however, has a marked depressing effect on the absorbance of the coloured solution; its content, therefore, must be carefully controlled and duplicated exactly in the blank solution. This is the reason for adding it from a burette.

4. Some of the reagents employed for the separation of magnesium affect the absorbance of the coloured sample solution. The preparation of a blank solution, to be

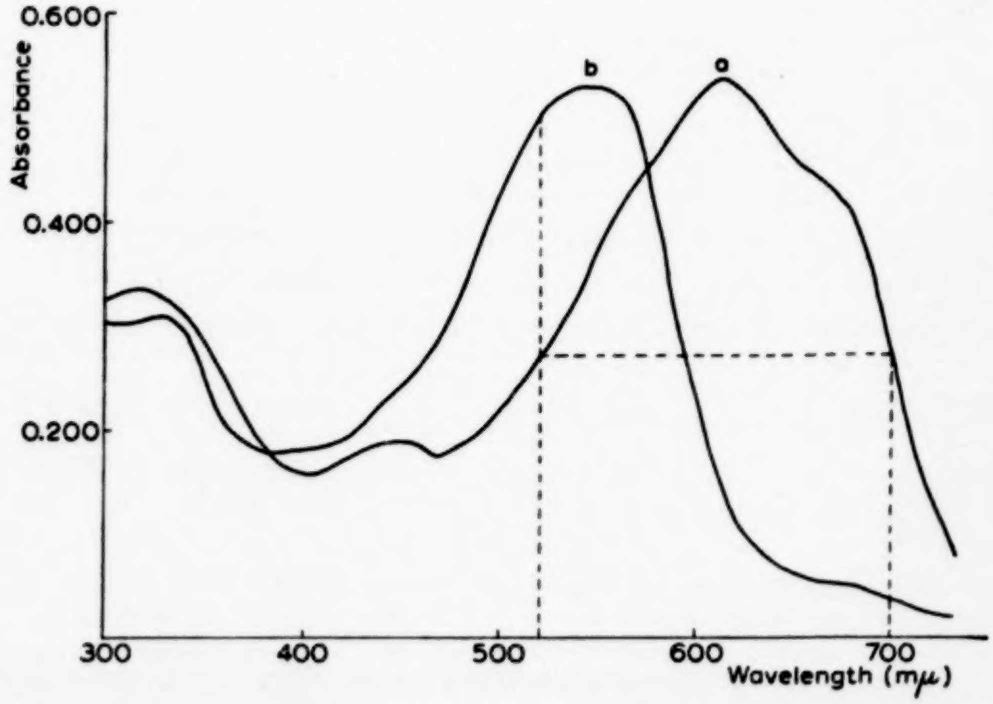

Fig. 2. Absorption spectra: a. 30 p.p.m. of Eriochrome Black T; b. 30 p.p.m. of Eriochrome Black T + excess Mg^{+2}.

carried through all the steps of the separation and subsequent colour development, is therefore essential.

5. From the start of these experiments, the salient factors affecting the development and the stability of the coloured solution were investigated. Stable and reproducible coloured solutions result, provided:

(a) The pH of the sample solution is 10.1[6] at the time of the addition of the reagent (Eriochrome Black T); this is ensured by the use of an appropriate buffer solution.

(b) The reagent is added with constant stirring.

(c) A large excess of reagent is employed.

6. Temperature changes of ± 5° have no discernible effect on the absorbance of the coloured solutions.

7. The absorbance of the coloured solutions does not change with time; absorbances measured at the time of the development of the colour were found to be unchanged after one hour.

8. The spectra of the reagent and of the magnesium - Eriochrome Black T complex, at pH 10.1, were each determined against distilled water (Fig. 2). It is evident from Fig. 2 that, while the absorption curve of the Mg^{+2} complex shows a maximum near 520 mμ, the reagent itself absorbs considerably at this wavelength; the absorbance of the complex must, therefore, be determined by a differential method, especially since a large excess of reagent is required. By drawing a horizontal line through the point of 520 mμ on the reagent absorption curve until it meets the curve again, another wavelength is found at which the absorbance of the reagent equals that at 520 mμ (see Fig. 2, dotted line; 702 in our experiments*). At this wavelength the absorbance of the magnesium - Eriochrome Black T complex is negligible, and the absorbance measured may be taken as resulting from the excess of Eriochrome Black T reagent present in the coloured sample solution. The difference between the absorbances measured at the two wavelengths (520 mμ and 702 mμ respectively) may therefore be taken as proportional to the amount of magnesium - Eriochrome Black T complex present in the sample solution**.

RESULTS

1. *Calibration curve*

This was constructed according to the directions given in section "D" of the PROCEDURE. Series of 10 replicate determinations were made with samples containing 20 γ to 70 γ Mg^{+2} per 100 ml (in 10 γ intervals). Table I summarizes the average values of the absorbances found and gives the maximum relative error for each Mg^{+2} content.

2. *Application to the analysis of alloys*

The alloys set out in Table II were analysed by the method described. Table III shows some of the results obtained.

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* Under PROCEDURE it has been recommended that the second wavelength be found experimentally in the range of 690 mμ to 710 mμ. No exact wavelength is given, as an experimental determination automatically compensates any small differences that might be caused by uneven calibration of the instrument or by small differences in the purity of the Eriochrome Black T.

** The points chosen for the absorbance measurements lie on the slope of the absorption curves; special care must therefore be taken to set the instrument scale as exactly as possible on the chosen wavelengths.

TABLE I

Mg^{+2} *per 100 ml*	*Absorbance*	*Maximum relative error* %
20	0.117	6.0
30	0.186	4.5
40	0.258	2.7
50	0.324	4.6
60	0.394	2.8
70	0.478	2.6

Beer's law is obeyed in the above concentration range.

TABLE II

COMPOSITION OF THE ALLOYS EMPLOYED TO CHECK THE METHOD *

Alloy No.	*Mg*	*Al*	*Cu*	*Fe*	*Mn*	*Si*	*Zn, Ni, Pb, Cr, Sn, Ti etc.*
1	10.57	the rest	0.03	0.18	0.06	0.10	traces
2	5.47	the rest	0.05	0.22	0.56	0.95	
3	2.00	94.00	4.00				
4	1.27	87.30	4.64	0.51		0.39	the rest
5	1.00	the rest					

* Alloys No. 1 and No. 4 were B.C.S. Standard Alloys No. 262 and No. 181 respectively; in alloy No. 2 magnesium was determined by the oxine method; alloys No. 3 and No. 5 were synthetic alloy solutions.

TABLE III

Alloy No.	*Magnesium theoretical* %	*Magnesium found* %	*Relative error* %
1	10.57	10.13	— 4.2
1	10.57	10.95	+ 3.6
2	5.47	5.29	— 3.3
2	5.47	5.53	+ 1.1
3	2.00	1.92	— 4.0
3	2.00	1.96	— 2.0
4	1.27	1.26	— 0.8
4	1.27	1.30	+ 2.4
5	1.00	0.98	— 1.7
5	1.00	1.01	+ 1.0

SUMMARY

The determination of magnesium in aluminium alloys by a differential spectrophotometric method is described. Magnesium is separated and the absorbance of its coloured complex with Eriochrome Black T measured.

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Received March 6th, 1958

SPECTROCHEMICAL DETERMINATION OF GERMANIUM IN TAR ASHES

by

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A relatively large number of methods for the spectrochemical determination of germanium in various materials has been described[1]; however, only the work of MARKS AND HALL[2] deals with samples having varying matrices.

MARKS AND HALL's method is one of "total energy", based on principles developed by SLAVIN[3]. Small, accurately weighed samples, buffered with lime–graphite mixture, are arced to completion, and line intensities are recorded on the photographic emulsion as on an integrating device, regardless of the volatilization rates of the matrix components.

Our attempts to make use of MARKS' general method proved unsuccessful, simply because no internal standard is used, so that no correction can be made for arc wandering, which causes corresponding shifts at the slit. It should be possible to eliminate arc wandering and corresponding variations of line intensities by optical[3], mechanical[4], or magnetic[5] devices; however, it was considered useful to develop a method using internal standardization, which would be just as effective for samples having varying matrices as the total-energy methods (which do not use internal standardization). An additional fact favouring the development of such a method is the necessity of accurately weighing samples, and quantitatively filling the electrodes in total energy methods; this has recently led FRISQUE[6] to develop a general method using internal standardization.

EXPERIMENTAL

A quartz-prism spectrograph was used in this work, the plate factor of which was 9 Å/mm in the wavelength range of 2500 Å. The source was an electronic rectifier with 100–300 V output. Medium-speed emulsion plates were employed throughout, while Kodak D-19; and Kodak F-5 were used in the photographic process. A Zeiss microphotometer was utilized in order to evaluate the optical densities of the lines concerned.

The 5-mm diameter graphite cathode was of the "normal shape", a crater of 3 mm depth and 2.5 mm diameter was drilled into the anode.

In view of the facts mentioned below, the following arcing conditions were selected:

Slit width	0.0175	mm	Height of intermediate image diaphragm	1.2	mm
Electrodes gap	9	mm	Exposure	the first 4 min of arcing	
Voltage (D.C.)	300	V	Analysis pair	Ge I 2651.178 Å – Fe I 2645.427 Å	
Current (regulated by means of a 25 ohm ballast resistance)	9	A			

References p. 504

The arc temperature was kept independent of the matrix elements by buffering with $CaCO_3$. Because of possible cathode- and anode-effects, the light was taken from the centre of the arc only. The distance between the electrodes was kept constant and checked optically (using a three lense system with an intermediate image). In order to convert the optical densities to line intensities, and to make the correction for background if necessary, each plate emulsion was calibrated by means of a 7-step weakener. Any line in the wavelength concerned can be used in connection with the weakener, since gamma only on the plate is to be known (Fig. 1).

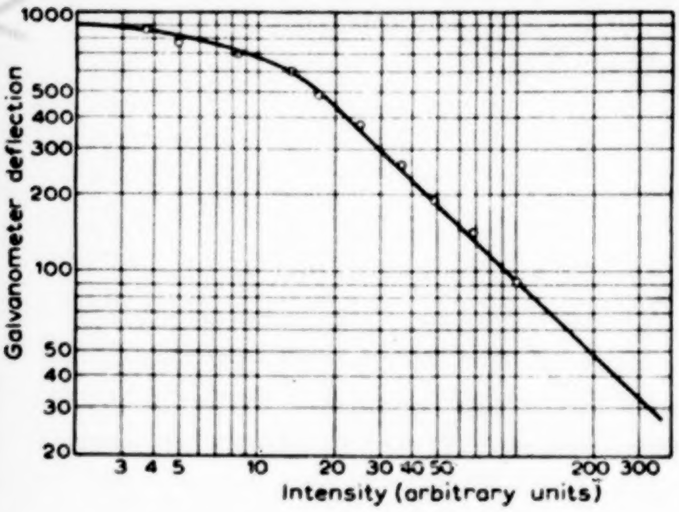

Fig. 1. A typical calibration curve. The curve is constructed from the transmission values of a 7-step weakener, using the lines Fe 2645.427, and Fe 2644.000 Å.

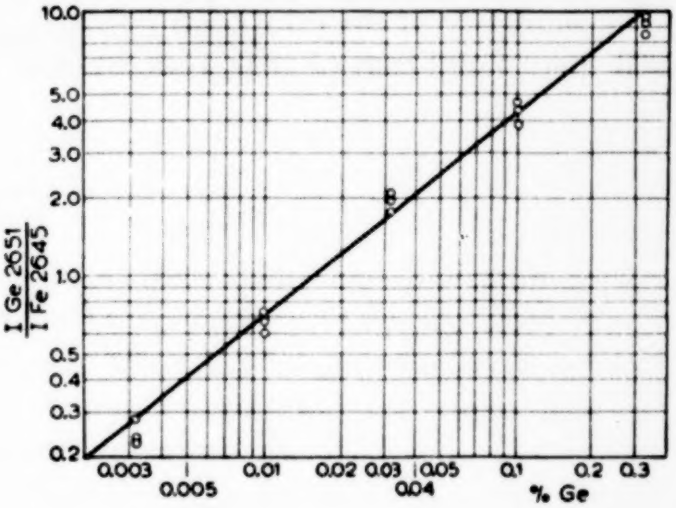

Fig. 2. Working curve. No correction for background has been made in this case.

The analytical curve (Fig. 2) was plotted using the intensity values of the lines concerned of standards prepared from pure GeO_2 and a matrix containing 71.3% Fe_2O_3 and 28.7% SiO_2. Before arcing, each standard was mixed with equal parts of graphite and $CaCO_3$.

The tar ashes had, of course, various Fe contents. It should be possible to make use of the variable internal standard method[7,8], but another procedure was worked out in order to equalize the sample matrices simultaneously.

The Fe content, determined beforehand by chemical wet analysis, was brought to 50% with pure Fe_2O_3 (the Fe being present as Fe_2O_3, as a consequence of the method of ashing). If a sample contained, *e.g.*, 10% Fe_2O_3, the amount of Fe_2O_3 to be added to 0.1 g of sample could be computed from the equation

$$\frac{0.01 \times 0.7 + 0.7x}{0.1 + x} = 0.5$$

0.315 g of sample diluted with Fe_2O_3 was thus obtained, to which equal parts of graphite and $CaCO_3$ were added. After homogenization, the samples were analysed spectrographically. The percentage found had only to be multiplied by the factor $(0.1 + x)/0.1$ (where x = the amount of Fe_2O_3 added) to obtain the correct result.

TABLE I

Sample No.	*Ge, found chemically* %	*Ge, found spectrochemically* %
1	0.075	0.080
2	0.921	0.902
3	0.009	0.013
4	0.054	0.060
5	0.321	0.322
6	0.012	0.019
7	0.016	0.018

References p. 504

RESULTS

Although the composition of the ashes differed perceptibly, the amounts of the main components Fe and Si varying from 3–30%, and 10–20%, respectively, and the remaining components differing even qualitatively, the results found spectrochemically compared favorably with those obtained chemically (Table I).

The precision of the method is 8.6%, expressed as standard deviation. Owing to the similarity of the excitation potentials of the lines used, the intensity response of Ge 2651.2 and that of 2645.4 are in close agreement (Fig. 3).

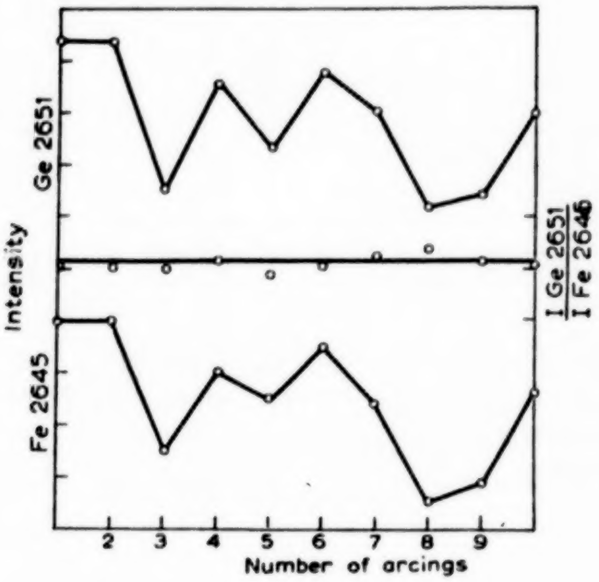

Fig. 3. The convenience of the analysis pair used. Though some of the conditions of arcing were changed deliberately, the ratio *I* Ge/*I* Fe remained close to the mean value (*i.e.* the line parallel to the abscissa).

SUMMARY

A technique for the emission spectrographic determination of germanium in tar ashes is described. Internal standardization was employed, Ge 2651.178 Å, and Fe 2645.427 Å being the analysis pair. The effects of varying matrix were diminished by making up the Fe contents of the samples to a convenient limit, and by the addition of calcium carbonate. The technique, applicable to materials of reasonably different matrices, gives a precision of the order of 8–9%, expressed as standard deviation.

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Received March 17th, 1958

Short Communication

Effect of heating rate on the melting point of amine tetraphenylboron derivatives

The use of the tetraphenylboron ion for the qualitative identification of amines[1-3], biogenetic amines[4-6], antibiotics[7], and alkaloids[8,9] has previously been studied. The nitrogen containing compounds gave immediate, water-insoluble precipitates, when contacted with aqueous solutions containing this ion. After drying, the amine derivatives were reported to give fairly sharp melting points.

We have found that the melting points of the amine derivatives are, in many cases, strongly dependent on the heating rate. Previous thermobalance studies[10] have shown that the amine derivatives began to lose weight at much lower temperatures than the literature values, indicating that extensive decomposition of the compounds took place before they melted. Hence, the dependence of melting point on the heating rate could probably have been expected. To our knowledge, no one has previously reported this phenomena so we wish to report our observations at this time.

Derivatives were prepared from 10 amines and 2 alkaloids as previously described[1]. It was found that having an excess of the amine or an excess of $NaB(C_6H_5)_4$ present during the precipitation process did not alter the melting point of the derivatives. Recrystallization of the derivatives from various organic solvents was found, in some cases, to cause decomposition. Hence, the melting points were determined on uncrystallized derivatives. The melting points were determined in an oil bath of 250 ml capacity, electrically heated, and stirred by a constant speed electric motor. The heating rate of the bath was controlled by varying the heater input voltage by means of a variable voltage supply. All melting points were taken in 1-mm capillary tubes, using sample sizes ranging from 5-15 mg in weight.

The procedure for taking the melting points consisted of first preheating the bath to about 10° below the melting point of the derivative. The melting point tube was then immersed into the bath and the bath temperature raised to the melting point at a controlled heating rate. The temperature of the bath was measured with a calibrated thermometer but stem corrections were not applied.

The dependence of the melting points on the heating rate is given in Table I. It can be seen that in some cases, the melting point values found differed considerably from the literature values. However, in most cases, the literature values fell within the heating rates studied, although the melting points sometimes covered a 14° range.

The melting points of the lower aliphatic amines seemed to be most dependent on the rate of heating, while the higher molecule weight amines were less dependent. The benzylamine derivative had only a 2° temperature variation over the entire heating rate range. For the two alkaloids studied, there was little variation in the

TABLE I

EFFECT OF HEATING RATE ON THE MELTING POINT OF AMINE TETRAPHENYLBORON DERIVATIVES

Amine	*Reported m.p.*	*Heating rate, °C/min*							
		2	*4*	*6*	*8*	*10*	*12*	*14*	*16*
Methylamine	209–11[a]	203–5	204–7	206–8	213–15	212–14	212–14	215–18	
Dimethylamine	157–61[a]	170–2	172–4	180–3	181–4	181–4	180–2	182–5	183–5
Trimethylamine	170–2[a]	153	153	156	161	159	161	168	165
Diethylamine	169–70[a]	166	169	172	174	176	180	181	184
n-Butylamine	126.5–8.5[a]	127–8	132	133–4	135–7	137–8	140		
Benzylamine	178–82[a]	134	134	134	134	134	135	136	136
Guanidine	177[d]	173	173	173	175	175	175	175	176
Quinoline	135–7[a]	133	134	133	134	135	135	136	136
Hexamethylenetetramine	160–1[a]	158	159	160	161	162	162	164	164
Brucine	144–5[b] 156–8[c]	143	144	144	145	145	147	148	149
Caffeine	128–9[a]	128	129	130	130	129	131	133	136

[a] Reference 1
[b] Reference 8
[c] Reference 9
[d] Reference 4

melting points with heating rate; however, the literature values did not agree very well with each other in the case of brucine.

It can be concluded from this study that caution should be exercised when using the amine tetraphenylboron derivatives for qualitative identification purposes. Since the melting points depend on the heating rate in many cases, the rate of heating should be taken into consideration. Other methods should always be used to confirm the results found with the tetraphenylboron derivatives.

ACKNOWLEDGEMENT

The helpful advice of Dr. Joe A. Adamcik is gratefully acknowledged.

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Received June 30th, 1958

REVUES DE LIVRE

Trace Analysis par John H. Yoe, John Wiley and Sons Inc., Publishers, New York, 1957, 672 p., relié, $ 12.—.

Les auteurs de cet ouvrage ont assemblé les exposés présentés dans un symposium traitant de l'analyse des traces et tenu à l'Académie de Médecine de l'Université de New York en novembre 1955.

Chacun sait l'importance de ce problème dans la plupart des domaines de la science moderne et les difficultés qui surgissent lors de ces délicates déterminations, aussi cette mise au point venant des plus grands spécialistes anglo-saxons sera-t-elle précieuse aux chimistes comme aux biologistes.

Ce livre est subdivisé en trois parties d'inégale importance. La première, et la plus vaste (547 p.), est intitulée méthodologie, elle comprend la chromatographie, l'électrochromatographie, les échangeurs d'ions, l'extraction, la microscopie chimique, l'analyse à la touche, la colorimétrie, la fluorimétrie, la spectrographie de flamme, la potentiométrie, la coulométrie, la polarographie et la voltammétrie, l'ampérométrie, la spectrographie, la spectrométrie gamma et la spectrométrie par rayons X, l'analyse par activation aux neutrons et enfin les techniques microbiologiques (ions inorganiques).

Chacun de ces chapitres comprend un bref rappel du procédé et de l'appareillage étudiés, puis l'auteur montre comment il faut procéder lorsqu'il s'agit de doser des traces de substances. Dans chaque cas, les limites de précision et de sensibilité sont données, on en explique les raisons. Les possibilités de chaque appareil sont soigneusement examinées et de nombreux exemples viennent illustrer ces divers exposés.

La deuxième partie, dite „instrumentation", donne un certain nombre de renseignements sur la construction de quelques dispositifs utilisés dans l'analyse et la dernière partie apporte d'intéressantes précisions concernant les séparations et la contamination, problèmes fondamentaux dans le dosage de traces.

Si cet ouvrage n'a pas l'homogénéité d'un livre conçu par un seul auteur, il présente par contre le grand avantage d'être présenté par des hommes rompus aux difficultés de l'analyse, connaissant à fond le sujet qu'ils traitent. La lecture de cet ouvrage est bénéfique, d'abord parce que les exposés y sont bien présentés, bien ordonnés, dépouillés de tout bavardage inutile, puis parce qu'il montre

que l'analyse des traces est une opération pleine d'écueils que seul un chimiste averti peut mener à bien. Il évitera aux trop nombreux amateurs des expériences malheureuses. Un beau livre à recommander aux analystes et à tous ceux que le problème intéresse.

D. MONNIER (Genève)

Modern Electroanalytical Methods, Proceedings of the International Symposium on Modern Electrochemical Methods of Analysis, Paris, July 1957. Edited by G. CHARLOT, Elsevier Publishing Company, Amsterdam, 1958, xii + 184 p., 36 tables, 124 ill. £ 1.4.—.

Une des conséquences de l'évolution rapide qu'a présentée l'électrochimie au cours des soixante dernières années, est la mise au point de nombreuses méthodes d'analyse; celles-ci sont basées sur les phénomènes les plus divers qu'accompagnent le fonctionnement d'une électrode et appelées, en général, méthodes d'analyse électrochimique.

L'électrochimie étant encore en plein développement, l'analyste, de nos jours, se voit obligé de suivre quotidiennement la bibliographie, afin de pouvoir profiter des derniers progrès apportés dans ce domaine. Tâche plutôt pénible et souvent infructueuse, car elle demande trop de temps et surtout une longue expérience, avant que l'on puisse se rendre compte de la valeur réelle d'une nouvelle méthode.

Or, le *Modern Electroanalytical Methods* vient précisément remédier de son mieux à ce mal du siècle. Publié sous la direction du Professeur CHARLOT, dont le nom seul suffit pour garantir l'importance d'un ouvrage, ce livre est le recueil complet des communications scientifiques présentées au Colloque sur les Méthodes Electrochimiques Modernes d'Analyse (Rappelons que ce colloque s'est tenu à Paris en juillet 1957, dans le cadre du Congrès de l'U.I.C.P.A.).

D'éminents spécialistes exposent dans le volume en question les développements les plus récents réalisés dans le domaine de l'analyse électrochimique. Le lecteur y trouvera aussi bien des exposés de caractère général que des exposés ayant trait aux applications pratiques, comme par exemple le dosage de traces de métaux par des méthodes polarographiques spécialement modifiées. Ajoutons encore que chaque conférence est suivie d'une discussion critique.

Il ne nous est malheureusement pas possible de passer ici en revue tous les communiqués. Aussi, nous contenterons-nous d'en citer les titres: Chronopotentiometry in fused lithium chloride–potassium chloride. Ampérométrie avec deux électrodes indicatrices. Potentiométrie à intensité constante. Courbes intensité–potentiel dans les échangeurs d'ions. Coulometric determinations. The millicoulometric method for *n*-values. Coulometrie und das Coulomb als universelle Urtitersubstanz. Adsorption kinetics and electrode processes. New techniques in radiochemical determinations using polarographic methods. Anodic stripping voltammetry with mercury electrode. Potential step and current-step methods. Factors to be considered in quantitative polarography with the rotated dropping mercury electrode. The use of the rotated dropping mercure electrode in polarographic analyses and amperometric titrations of micromolar solution. Application de la goutte pendante de mercure à la détermination de minimes quantités de différents ions. Current scanning polarography at the dropping mercury electrode. Square wave polarography and some related techniques. Oszillopolarographische Mikroanalyse. Polarographische Untersuchungen cytostatischer Chinonderivate. Polarographie und Oszillographie des Vitamins B_1 vom analytischen Standpunkt. Anwendungsmöglichkeiten der Hochfrequenzmesstechnik in der analytischen Chemie. Titrimètre à haute fréquence; utilisation pour les titrages en milieu anhydre. Newer methods of determining electrolytic conductivity. Neue Theorie der Electrolyse und der Redoxydationen.

Nous ne saurions terminer ce compte rendu sans y relater l'excellente présentation de l'ouvrage que nous tenons à recommander chaudement, tant aux analystes qu'aux électrochimistes, persuadés qu'ils pourront y puiser abondamment de sujets fort intéressants et de toute actualité.

I. KAPETANIDIS (Genève)

ANNOUNCEMENT

The XVIIth International Congress of Pure and Applied Chemistry is to be held in Munich, 26th–29th August, 1959.

Readers wishing to receive the circular giving general information about the Congress are invited to write to: Generalsekretariat des XVII Internationalen Kongresse für reine und angewandte Chemie, München 2, Meiserstrasse 1 (Deutschland).

ION EXCHANGE SEPARATION OF METAL IONS*

by

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Because there are limitations to the selectivity attainable by most analytical methods, preliminary separations must frequently be employed. Ion exchange methods are attractive provided that quantitative separations can be achieved quickly and without excessive manipulation. The method studied in this paper depends on the selective complexation of metal ions by EDTA [(ethylenediamino)-tetraacetic acid]. Selectivity is achieved by proper choice and control of pH. The uncomplexed metal ions are retained by a short cation exchange column, while the complexed metals pass quantitatively through the column. This type of separation has already been used by a few investigators[1-8].

In this paper quantitative ion exchange separations are attained quickly because a short (4-cm) column is used. Excellent pH control is effected by incorporating a buffer in the sample to be separated, and by treating the resin column with the same buffer solution. The ion exchange retention of several metal cations in EDTA solution was studied as a function of pH. From the behavior of individual ions, predictions can be made as to the mixtures that can be separated by this method. Several actual separations are reported.

THEORETICAL PRINCIPLES

Metal–EDTA complexes, in common with most metal organic complexes, become weaker as the acidity of the solution is increased. The formation constants indicate the relative strength of EDTA complexes, and it follows that with decreasing pH the various metal–EDTA complexes will be broken up in the order of their formation constants. If the formation constant of M_1–EDTA is appreciably greater than M_2–EDTA, adjustment of the pH to the proper value will result in M_1 remaining firmly bound in a neutral or anionic EDTA complex, while the M_2 complex will be appreciably dissociated. If the mixture is passed through a cation exchange column under conditions where the chosen pH will be maintained, M_2 will be taken up by the column while M_1 will pass through the column as the EDTA complex. For the separation to be quantitative the difference in formation constants should be 10^3 or greater.

The pH at which a metal complex dissociates may be calculated from the formation constant of the complex, from the acid dissociation constants of the complexing agent and from the distribution coefficient D of the metal ion between the resin and the aqueous phase.

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* Contribution No. 600. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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The value of D varies considerably with the charge on the metal ion. A rough estimation of D (for resin charged with a $+1$ cation) is 1 for $+1$ ions, 10^2 for $+2$ ions, 10^4 for $+3$ ions and 10^6 or greater for $+4$ ions. As will be shown later, this variation in the value of D with charge has an important effect on the conditions and scope of ion exchange separations by the complex method.

The rough values of D permit approximate prediction of the pH required for any feasible separation. The exact pH range that is applicable, however, must be determined experimentally. One reason is that below pH 3, most metals form protonated EDTA complexes.

$$MY^{-4+n} + H^+ \rightarrow MHY^{-3+n} \quad \text{. . . . .} \quad (1)$$

The formation constants for these complexes are not very accurately known. Also there is some question as to the acid dissociation constants of EDTA. In glacial acetic acid, EDTA combines stoichiometrically with a proton.

$$H_4Y + H^+ClO_4^- \rightarrow H_5Y^+ ClO_4^- \quad \text{. . . . .} \quad (2)$$

This reaction probably takes place in aqueous medium too, but no equilibrium constant has ever been reported for the reaction. Finally, the distribution coefficients cited above are only estimated; also it is not known how many theoretical plates are involved in the ion exchange step of the separation.

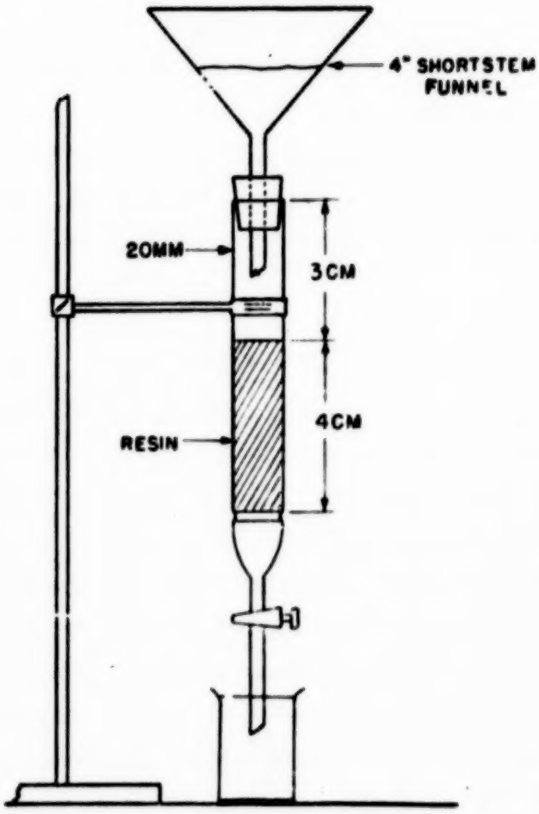

Fig. 1. Ion exchange column.

EXPERIMENTAL

Apparatus

A Beckman model G pH meter equipped with Beckman 1190-80 glass and 1170-calomel reference electrodes was used for all pH measurements. A Beckman model B spectrophotometer with 1-cm borosilicate glass cells was used for all spectrophotometric measurements. Three ion-exchange columns as illustrated in Fig. 1 were used for all work except where the effect of column length was investigated. For that purpose similar columns were used, but the height from the glass frit to the top of the column was 13 cm. The columns were fitted with a 60° funnel with a top diameter of about 8 cm.

Reagents

Dowex 50-X4 (50–100 mesh) nuclear sulfonic acid type cation exchange resin in the sodium form was used throughout this work except for investigation of the effects of varying crosslinkage. Elution with sodium citrate was employed to remove impurities from the resin before using it for the first time. All resin was rinsed with ethanol and acetone, and then air dried before use. All other chemicals used were of reagent grade or higher purity.

Solutions

EDTA (0.05*M*). Dissolve 18.6 g of reagent grade EDTA in one liter of water. Standardize against a standard zinc solution or against primary standard calcium carbonate. A second 0.05*M* EDTA solution is prepared in the same manner, but is not standardized. This solution is used to add to the samples before passing them through the resin columns. Since an excess of EDTA is used here, rigorous standardization is not necessary.

Glycine (0.2*M*). 60 g of glycine is dissolved in 4 l of water. 4 g of phenol is added to inhibit mold growth in the solution during prolonged storage.

Formic acid (0.2*M*). 30 ml of 98–100% formic acid diluted to 4 l with water.

Buffer solutions. The appropriate acid solution (0.2*M* glycine for pH 1.0 to 3.6, 0.2*M* formic acid for pH 2.7 to 4.2, or mineral acid for pH less than 1.0) was poured into a 1-l beaker to within 2.5 cm of the top. Fifty ml of the unstandardized 0.05*M* EDTA solution was measured out in a graduate cylinder and added to the buffer. The pH was adjusted with hydrochloric acid, nitric acid or ammonium hydroxide to the desired value, using a pH meter.

Metal ion solutions (0.05*M*). The required amount of the metal, or the salt or oxide of the metal, is dissolved in water or acid, as required, and diluted to 1 l with water.

PROCEDURES

The procedures used to obtain the data to be presented were essentially the same for all the metal ions studied. Since many factors affect the systems investigated here, rigorous attention to the mechanical details of the procedures must be maintained.

Preparation of the ion exchange column

Five g of air-dried Dowex 50-X4 resin was weighed on a triple beam balance and poured into each of three ion-exchange columns which contained water to a depth of about 4 cm with the funnels removed. After the resin had settled and swelling had ceased, the columns were tapped lightly to level the resin. The funnels were inserted so that the tip of the funnel was about 1 cm above the water level. The funnels on top of the ion exchange columns were filled with buffer solution, and the solution was passed through the columns at a rate of 10–15 ml/min, regulated by the stopcock on the bottom of the column. The effluent solution was collected in a 250-ml beaker until the solution level had fallen to the top of the neck of the funnel. The pH of this effluent solution was then measured. If it was within 0.1 unit of the desired pH value, the column was ready for use. If the pH was off by an amount greater that 0.1 unit, more buffer was passed through the column until a fresh portion of effluent had the desired pH.

Separation of the sample

To a 10-ml aliquot of the 0.05*M* metal ion solution in a 150-ml beaker, 30 ml of the buffer solution and 15 ml of the unstandardized 0.05*M* EDTA solution were added. Using a pH meter, the pH of the sample was adjusted to the desired value with the appropriate acid or ammonium hydroxide. When the correct pH had been attained, the sample was poured into the funnel at the top of the column, and passage through the column was started immediately with the rate of flow controlled by the stopcock within the range of 8–11 ml/min. The effluent solution was collected in a

250-ml beaker. When the level of the sample solution in the funnel had dropped to the top of the neck of the funnel, a 30–40 ml rinse of the buffer solution was poured into the funnel without stopping the flow of solution through the column. This process was repeated two additional times with each sample, giving a total volume of 90–120 ml of effluent in addition to the volume of the original sample. The effluent solution was retained for analysis as described in the next section.

When the portion of the sample that was retained by the column was of interest, it was eluted by passing 90 ml of a $4N$ hydrochloric acid solution through the column at a rate of $1^1/_2$–2 ml/min. The effluent solution was collected in a 150-ml beaker and retained for analysis as described in the next section.

Analysis of samples

Since the preferred method of analysis, wherever applicable, was titration with EDTA, the removal of the EDTA and other complexing substances present in the sample was imperative. This was accomplished through the use of a wet ashing with nitric and perchloric acids. The principles of this process are very adequately treated by SMITH[9].

The methods used for analysis of the various metal ions were as follows:

Thorium: Thorium was analyzed by titration with EDTA using the method of FRITZ AND FORD[10]. The indicator used was a mixture of equal volumes of 0.2% alizarin red S and 0.1% bromcresol green solutions instead of the 0.2% alizarin red S solution recommended by the authors.

Rare earths, scandium and yttrium: These metals in $0.05M$ and $0.005M$ concentrations were analyzed by the method of FRITZ, OLIVER AND PIETRZYK[11] using titrant of equivalent molarity. Colorimetric analyses of microgram amounts were carried out by the method of FRITZ, LANE AND RICHARD[12] using the Beckman model B spectrophotometer.

Copper and zinc: Copper and zinc were analyzed by the method of FRITZ, LANE AND BYSTROFF[13].

Zirconium: Zirconium was analyzed by the method of FRITZ AND JOHNSON[14].

Iron: Iron was analyzed by titration with EDTA. Sulfosalicylic acid was used as indicator, and the titration was carried out at pH 2.0–2.5. The end-point was taken as the last discernible change in color from red through yellow-orange to the pale yellow green of the iron(III)-EDTA complex.

RESULTS

Table I and Fig. 2 summarize the data obtained for the distribution of metal ions between resin and solution as a function of pH when the samples are treated by standard conditions of the procedures given above. All of the results were obtained using 5 g of X4 resin in the column with flow rates all in the range of 8–11 ml/min.

A study of the curves in Fig. 2 shows the importance of the valence effect discussed in an earlier section. For example the formation constants of the EDTA complexes of zinc and samarium are almost identical, yet samarium is taken up by the ion exchange column at a significantly higher pH than zinc. This is because the resin has a greater affinity for samarium, a trivalent ion, than it has for a divalent ion such as zinc. Another illustration of this point is provided by the thorium and ytterbium

TABLE I

RETENTION OF METAL IONS AS A FUNCTION OF pH

pH	*Metal ion*	*% on column*	*Buffer[a] used*	*pH*	*Metal ion*	*% on column*	*Buffer[a] used*
0.9	Th	100.0[b]	HCl	0.9	Yb	100.0	HCl
1.2	Th	87.5[b]	GH	1.2	Yb	99.5	GH
1.5	Th	47.3[b]	GH	1.5	Yb	47.6	GH
1.8	Th	3.3	GH	1.8	Yb	0.9	GH
2.1	Th	0.1	GH	2.1	Yb	0.1	GH
0.6	Sc	61.9	HCl	0.6	Cu	15.9[b]	HNO_3
0.9	Sc	46.4	HCl	0.9	Cu	4.2[b]	HNO_3
1.05	Sc	0.3	GH	1.2	Cu	0.0[b]	GN
1.2	Sc	0.0	GH	0.6	Fe	0.0	HNO_3
1.5	Y	100.0	GH	1.2	Zn	99.1	GN
1.8	Y	94.6[b]	GH	1.5	Zn	83.5	GN
2.1	Y	60.2[b]	GH	1.8	Zn	39.4[c]	GN
2.4	Y	10.0[d]	GH	2.1	Zn	0.0[c]	GN
2.7	Y	2.4[d]	GH	0.6	Zr	5.5[b]	HCl
3.0	Y	0.0	GH	0.9	Zr	0.8[b]	HCl
2.1	Sm	100.0[d]	GH	2.7	La	100.0	GH
2.4	Sm	75.5[d]	GH	3.0	La	92.0	F
2.7	Sm	42.3[c]	GH	3.3	La	70.4	F
3.0	Sm	13.9	GH	3.6	La	18.6	F
3.3	Sm	0.1	F	3.9	La	0.0	F

[a] The designations of the buffer solutions are as follows: GH for glycine buffer acidified with HCl; GN for glycine buffer acidified with HNO_3; F for formic acid buffer adjusted with ammonia.

[b] Average of only 2 samples.

[c] pH of effluent solution less than 0.1 unit above the stated value.

[d] pH of effluent solution less than 0.2 unit above the stated value.

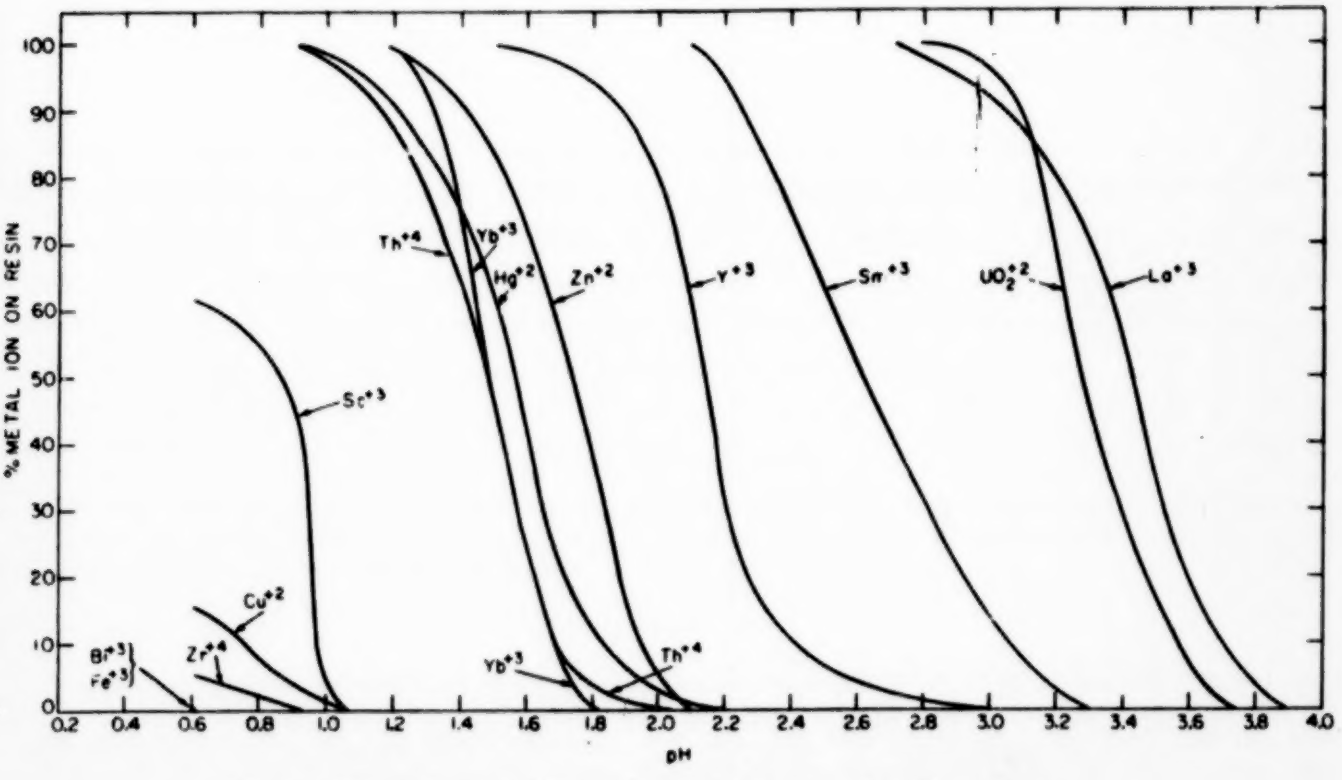

Fig. 2 Retention of different metal ions as a function of pH.

curves, which are almost identical despite the fact that the log *K* of thorium–EDTA is 23.2 while the log *K* of ytterbium–EDTA is only 19.5.

An examination of Fig. 2 will also suggest a number of interesting and practical separations. It should be possible to separate any of the rare earths from scandium, iron(III), bismuth or copper. At pH 2.0, rare earths through samarium can be separated from thorium, ytterbium or lutetium. A complete separation of thorium from iron or bismuth and a nearly complete separation of thorium from zirconium or scandium should be possible. Any of the metals listed can be separated from calcium, strontium, barium or magnesium, which are completely taken up by the resin column at pH 4.4.

Data for some actual separations are presented in Table II.

TABLE II

SEPARATION OF METAL IONS[a]

	Metal added mmol	*Metal found mmol*		*No. of samples*	*pH*
		On resin	*Through column*		
La	0.2424	0.242_9		3	2.2
Th	0.2484		0.2474		
Sm	0.245_9	0.2454		3	1.8
Fe	0.2474		0.2474		
Y	0.244_8	0.2450		3	1.35
Sc	0.258_0		0.2577		
Mg	0.996_2	0.996_9		2	4.0
Al	0.9994		not analyzed		

[a] Glycine buffer acidified with HCl was used in all cases except the Mg–Al mixture which was unbuffered.

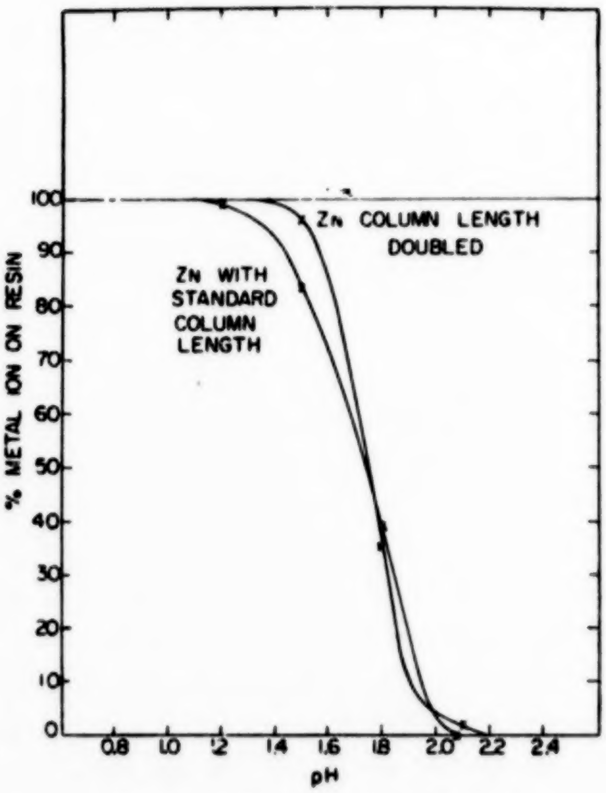

Fig. 3. Effect of column length.

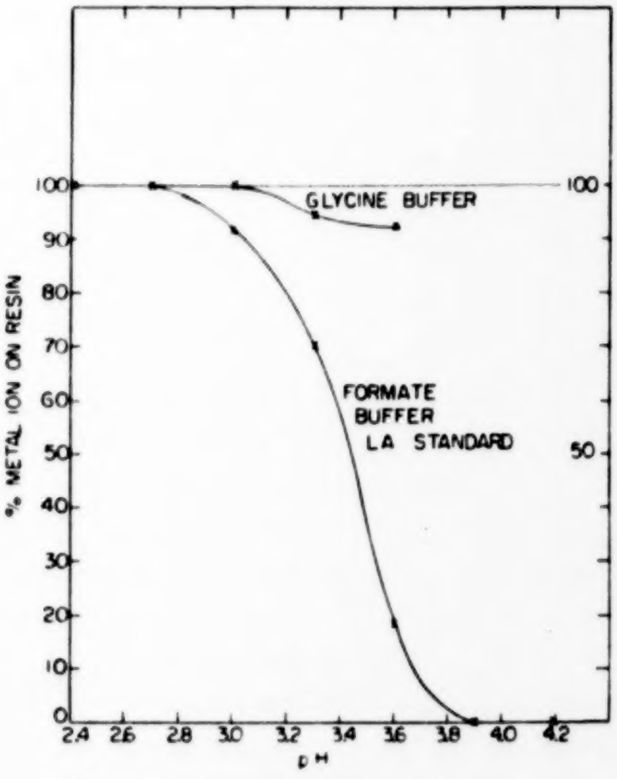

Fig. 4. Complexing effect of buffer.

DISCUSSION

One point that has been demonstrated is that successful separations can be obtained without resorting to the use of long columns. As shown in Fig. 3, doubling the column length does result in a slightly more abrupt retention–pH curve. However, it is more difficult to achieve precise pH control with a longer column.

Figs. 4 and 5 show some anomalous results obtained with glycine buffer. It may be that glycine starts to form some kind of a cationic complex with rare earths and EDTA above pH 3. Below pH 3.0, glycine is an excellent buffer for this type of ion-exchange separation.

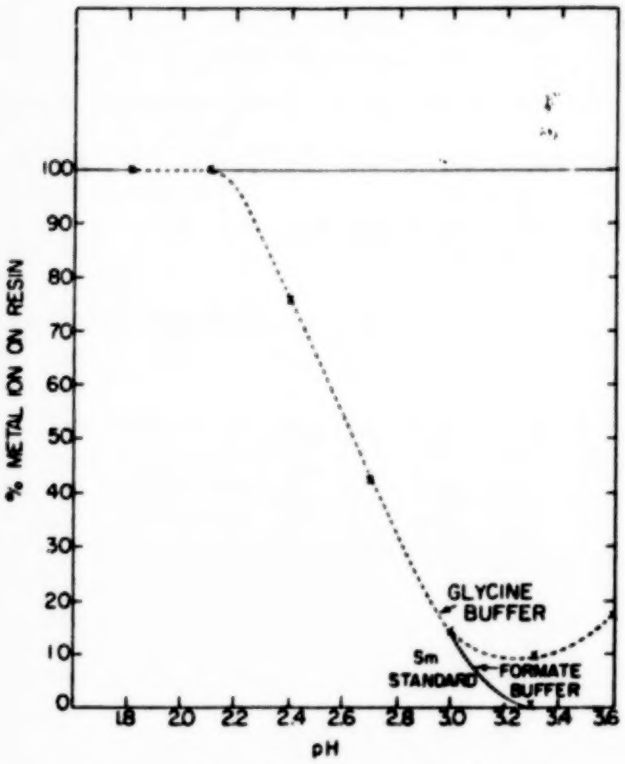

Fig. 5. Complexing action of buffer.

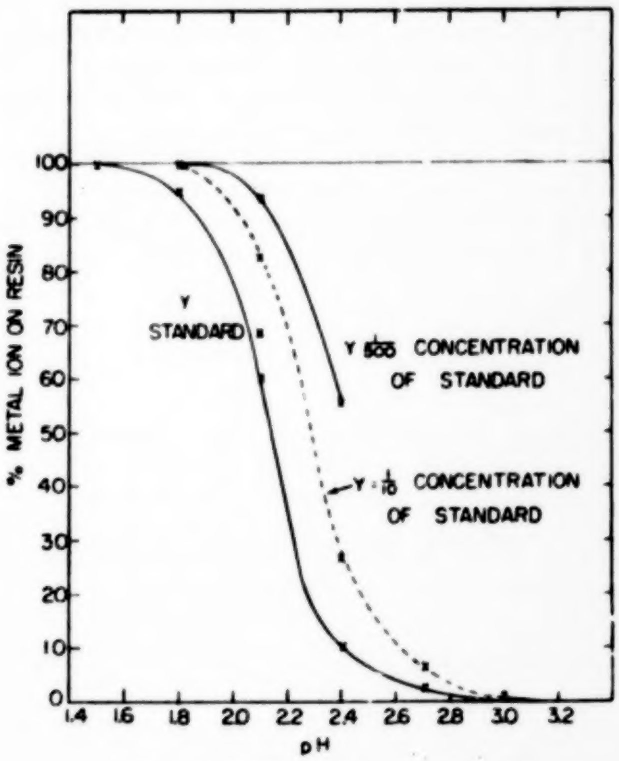

Fig. 6. Effect of concentration.

Other studies showed that faster flow rates cause undesirable "tailing" of the curves of retention *vs.* pH. Use of X-16 resin gave results similar to X-4 resin but also produced a very slight "tailing" effect. Varying the concentration of metal ions causes only a small displacement of the curve (Fig. 6). This suggests the possibility of separating and determining traces of a metal ion from a higher concentration of a more strongly complexed ion. This possibility is being investigated.

ACKNOWLEDGEMENTS

We wish to express our appreciation to THOMAS A. PALMER for his work on the ion-exchange behavior of bismuth. We also thank Dr. JACK POWELL and Dr. F. H. SPEDDING for the pure rare earth salts used in this investigation.

SUMMARY

A rapid ion-exchange method is proposed for the separation of several metal cations. The method depends on the selective complexing of metal ions by a chelating agent as achieved by control of pH. To accomplish this separation, an excess of EDTA [(ethylenediamino)tetraacetic acid] is added to the metal ion solution. The solution is buffered at a pH where the EDTA complex of one metal is quantitatively formed, while the complex of the other metal ion is largely disso-

ciated. The solution is then passed through a previously buffered column containing Dowex 50-X4 cation exchange resin. The uncomplexed metal ion is quantitatively removed from solution by the resin while the complexed ion passes through the column. The method has been applied with good results to several binary mixtures of metal ions.

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Received March 11th, 1958

THE DETERMINATION OF BORON IN TREATED WOOD

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Boron compounds are extensively used as wood preservatives and the standard methods for the detection and estimation of boron given in the Code of Practice[1] have recently been examined. As a result these methods have been modified and a satisfactory schedule for combined detection and testing for conformity with the standard specification has been devised.

Boron is a non-staining preservative and spot testing is necessary to determine its presence in the wood. Further, the specification stipulates a minimum core retention of 0.20% boric acid and analysis is necessary to determine compliance or otherwise with the specification.

SPOT TESTING PROCEDURE

The standard spot testing reagent[1,2] consists of two solutions:

(a) 1% alcoholic extract of turmeric,

(b) 20 ml of concentrated hydrochloric acid diluted to 100 ml with ethyl alcohol and then saturated with salicylic acid.

It was found that better results were obtained with a 10% extract of turmeric and subsequently, that a clear differentiation according to approximate boron contents could be obtained with modified turmeric solution. Thus the following spot testing and semiquantitative estimation was developed.

Reagents. I. 10% alcoholic extract of turmeric. II. Solution (b) as above.

Procedure

1. Apply solution I by spraying or pouring to the dry cross-section of the sample to be tested and allow to dry.
2. Apply solution II similarly and allow to dry.

From the colour developed the approximate concentration of boric acid in the core can be estimated as indicated in Table I. McMullen[2] has suggested the use of 1% turmeric solution for rapid sorting and the colours obtained are also given in Table I. It is considered more desirable that the middle range of colours should be slightly above the specified concentration of 0.2% and for this reason the use of 10% extract of turmeric is preferred.

TABLE I

Colour 1% Extract			*Red*	*Brown*
Colour 10% Extract	*Bright Red*	*Brown Red*	*Yellow Brown*	*Yellow*
Approx. boric acid concentration %	0.30	0.25	0.25	0.10

The samples showing less than 0.25% are analysed chemically. This rapid sorting test is very useful since only about 10% of the received samples need to analysed. Further, the gradation in colour from the outside to the centre gives an excellent indication of the standard of treatment, high concentration gradients being indicative of an inadequate diffusion period or undue drying of the timber before treatment. The test is affected by the character of the surface and to get the best results, cross-sections should be cut slowly with a fine toothed saw giving a smooth surface.

This test has been found to be satisfactory for all species with the exception of fast grown pinus species, where the colour developed is much more intense. Modification of solution (b) to the following allows the use of the test for rough sorting as in the above technique.

3. Acid solution for testing with pinus species.

10 ml of concentrated hydrochloric acid are diluted to 100 ml with ethyl alcohol and 10 g of salicylic acid are dissolved in the resulting mixture.

ANALYTICAL PROCEDURE

Samples showing concentrations below 0.25% are analysed. The standard method[1] includes ashing of the ground sample in admixture with lime (as used in Eschka's mixture), dissolution of the ash in hydrochloric acid followed by filtration and dilution to a standard volume. Aliquots are withdrawn and titrated by the sodium hydroxide–mannitol procedure using bromothymol blue as indicator and a Conway microburette. The alkali concentration is adjusted such that 1.00 ml is equivalent to 0.50% boric acid in the 5-g sample ashed.

This procedure is lengthy and gives occasional erratic results which could be correlated with failures to ash completely at the specified temperature of 600°. Ashing in the presence of sodium hydroxide, sodium acetate and barium hydroxide with and without nitrates was studied and it was found that best results were obtained by wetting the sample with a barium hydroxide–nitrate mixture and ashing at 600°. A fine greenish white ash was obtained which was readily soluble. It now became possible to improve the precision of the determination by the titration of the whole sample ashed and the following procedure is now used. McMullen[3] in a similar study has reached the same conclusion.

Reagents. Barium hydroxide $7^1/_2\%$ + Nitric acid conc. 1%; Hydrochloric acid A.R., 1:1; Sodium hydroxide, 10%; Hydrochloric acid A.R., 1:40; 0.0808N NaOH, CO_2 free, standardized against standard boric acid solution; Mannitol; 0.05% bromothymol blue.

Procedure

Weigh 5.000 g of the oven-dried wood ground to pass a 40-mesh sieve into a 30-ml size silica or nickel crucible and add 10 ml of barium hydroxide solution mix to ensure thorough wetting of the wood and dry in oven at 105° for 2 h.

Transfer to furnace at 200° and ignite at 600° for 2 h. Remove sample from furnace, cool and wet the ash with distilled water. Then carefully acidify the residue in the crucible with excess 1 : 1 HCl. Wash the contents of the crucible through a No. 4 9-cm filter paper rinsing out crucible with further small amount of acid and hot water and wash residue on the filter paper with 3 portions of hot water. The filtrate and washing should total about 60 – 100 ml. Add 1 ml of bromothymol blue, neutralize with 10% NaOH, acidify with 1 : 40 HCl adding a few drops in excess. Fit a reflux air condensor to the Erlenmeyer flask and boil to remove CO_2 until condensate reaches within $^1/_2$ inch of the top. Cool to room temperature, rinse the condensor tube and titrate with standard NaOH using a 10-ml microburette until the indicator shows a clear blue. Add excess of mannitol and titrate again with standard NaOH until a clear blue is again reached. Ensure that excess mannitol is present by adding a further small amount. The solution should remain unchanged in colour. If not, add further NaOH until addition of mannitol produces no further change. The volume of alkali consumed after addition of mannitol is equivalent to the boric acid present.

RESULTS OBTAINED WITH THE METHOD

As a check on the new method, 5-g samples of the ground wood were taken and treated with known amounts of boric acid and analysed by the Lime Eschka and barium hydroxide methods. Ten replicate determinations were done for each concentration. The solutions used above were also analysed in replicate by new and old methods. In the latter case, 5-ml portions were diluted and suitable aliquots taken as in the standard procedure.

All results were statistically examined and the values so obtained are given in Table II.

TABLE II

STATISTICAL RESULTS

Level Solutions x	*Method*	$\bar{x}$	s^2	s_m	t
0.200	New	0.1998	$4.2\cdot10^{-7}$	0.002	1.00
0.200	Old	0.1870	$1.12\cdot10^{-4}$	0.0034	3.83[a]
0.500	New	0.5010	$1.48\cdot10^{-5}$	0.0012	0.83
0.500	Old	0.4790	$1.43\cdot10^{-4}$	0.0039	5.40[b]
Wood Samples					
0.200	New	0.1988	$3.02\cdot10^{-5}$	0.0017	0.69
0.200	Old	0.1815	$23.4\cdot10^{-5}$	0.0048	3.83[a]
0.500	New	0.4823	$3.82\cdot10^{-5}$	0.0020	9.05[b]
0.500	Old	0.4675	$9.58\cdot10^{-5}$	0.0031	10.50[b]

$$t = \frac{x \sim \bar{x}}{s_m}$$

[a] indicates significance at 1% level

[b] indicates significance at 5% level

CONCLUSIONS

Solutions

There is no evidence of bias with the new method. The old method shows a significant negative bias at both levels. The reason for the negative bias with the old method is most probably due to the fact that when bromothymol blue is used as an indicator, the strict stoichiometric equivalence cannot be used for the calculation of boric acid content. The old method takes no account of this fact.

The ratio of variance estimates are 26.6 and 9.6; both would be judged significant by the $F_{\max}$ test. They indicate principally the resultant effect of similar reading errors in both methods.

Wood samples

There is no evidence of bias with the new method at the 0.200% level. Negative bias is observable at both levels with the old method and at 0.500% level with the new method. The new method is however significantly less biassed than the old method at the 0.500% level.

Reliable estimates of variance excluding the titration variance above cannot be obtained but there is a suggestion that at the 0.200% level the new method of ashing is more precise.

Thus it may be concluded that the new method is an improvement on the existing method giving better recoveries and at the 0.200% level more precise results. Certainly the new method is a distinct improvement in technique and effects a considerable saving in operators time.

Statistical sources

(1) Symmetric t test tabulated by FISHER & YATES[4].
(2) The $F_{\max}$ test tabulated by HARTLEY[5].

ACKNOWLEDGEMENTS

The writer is indebted to Mr. W. G. WARREN, Biometrician, New Zealand Forest Research Institute, for the statistical analysis of the results, to Miss B. BOYD for carrying out the analytical determinations, the Forestry Commission, New South Wales, for permission to quote from their reports, and the Director of Forestry, New Zealand Forest Service, for permission to publish.

SUMMARY

The detection of boron in treated wood with turmeric is described. The determination of boron in treated wood by ashing in the presence of barium hydroxide followed by titration with sodium hydroxide in the presence of mannitol is described.

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Received April 8th, 1958

ELECTRO-CHROMATOGRAPHY IN THE SEPARATION OF IONS

VI. SEPARATIONS OF ZINC GROUP METALS

by

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Separation of the ions of the zinc group was first reported by STRAIN[1] by two-way and three-way chromatographic technique using a mixture of lactic acid and ammonia or ammonia and 2% triethanolamine as an electrolyte. MAKI[2] suggested the use of meta- and polyphosphates as complexing agents for the separation of ternary mixtures of ions of the type Ni-Co-Zn and Zn-Co-Ni and observed further that even a mixture of ammonia (4*N*) and ammonium tartrate (0.1 *M*) was effective for the separation of the elements of the zinc group.

Our studies on the separation of elements in qualitative analysis and partly reported[3] in Parts III to V of this series reveal that a complete separation of all the four ions with distinctly separated zones is not possible with common electrolytes. With potassium cyanide (pH 6.0), however, the four ions form separate zones with only a slight spreading of the zinc band over the cobalt band, the order being Ni-Zn-Co-Mn. Ammonia, potassium cyanide (aq.) and potassium cyanide mixed with bromine give only a ternary separation of the type Mn-Co-Ni, Ni-Co-Mn, Zn-Co-Mn and Mn-Co-Zn.

EXPERIMENTAL

Solutions of nitrates of the ions of zinc, manganese, cobalt and nickel were prepared so that a small drop (0.01 ml) of the mixture contained only 15 μg of each ion. The experimental technique followed was the same as reported in previous papers[3]. The electrolytes used were usually decinormal in strength except in a few instances where electrolytes of higher strength were preferred. 0.1 *N* potassium cyanide solution with bromine was prepared by dissolving the required amount of potassium cyanide in 5% (w/v) bromine solution in water.

In Table I, the ionic movements have been recorded. The movements of ions towards the anode and the cathode are shown respectively by a + and a — sign and the starting by the symbol :. The square brackets indicate that the ions enclosed therein have a portion of their migration zones in common. Though a fairly large number of separations appear to be feasible, only a few have been achieved, as given in Table II. The rest invariably formed diffuse overlapping bands perhaps due to some sort of mutual influence of the ions on their rates of movement.

DISCUSSION

From the ionic movements it is evident that the four ions have more or less the same tendency to form complexes. They are usually cationic with most of the common electrolytes, whereas in the presence of citrate, tartrate, oxalate, ammonium thiocyanate (*N*), potassium cyanide, alone or with bromine, and dimethylglyoxime anionic complexes are formed. Manganese, however, is cationic with sodium potassium tartrate and potassium cyanide. Zinc is anionic in caustic soda, sodium thiosulphate,

TABLE I

EFFECT OF ELECTROLYTES (0.1N) ON IONIC MOVEMENTS IN cm

Ions	HNO_3	HCl	H_2SO_4	H_3PO_4	KCl	KI	$NaNO_2$	$Na_2S_2O_3$	NH_4CNS	NH_4CNS (N)	NaH_2PO_4	NaH_2PO_4 (0.1N HCl)	NH_4OH	NH_4OH (5N)
Zn^{+2}	−4.7	−4.4	−5.7	−10.1	−6.7	−7.0	−7.2	+2.8	−3.5	+5.6	−7.6	−6.2	−0.5	−4.7
Mn^{+2}	−3.8	−5.1	−6.2	−2.5	−6.5	−12.1	−6.7	−4.2	−5.5	+11.2	−7.4	−4.5	−1.1	0.0
Co^{+2}	−4.4	−5.6	−4.6	−13.0	−8.2	−9.3	−6.0 −9.0	−4.4	−7.0	+3.0	−9.7	−5.1	0.0	−3.0
Ni^{+2}	−4.2	−6.0	−5.2	−14.4	−7.3	−6.6	−6.5 −8.8	−3.4	−5.9	+3.3	−9.0	−4.7	0.0	−7.1

Ions	*NaOH*	*KCN* (*aq.*)	*KCN* (*pH 6.0*)	$KCN + Br_2$	*Acetic acid*	NH_4 *acetate*	*Tartaric acid*	*NaKtartrate*	*Citric acid*	*Na citrate*	NH_4 *oxalate*
Zn^{+2}	+0.6	+12.3	−1.8	+5.1	−5.1	−5.1	−6.0	+0.6	−5.3	+4.5	+5.1
Mn^{+2}	−0.3	−0.2	−6.9	+1.0	−8.5	−7.6	−9.8	−1.2	−12.1	+1.9	+2.3
Co^{+2}	0.0	+10.0	−2.5	+2.6	−7.7	−7.0	−8.9	+1.7	−7.5	+4.1	+3.6
Ni^{+2}	0.0	+14.6	+12.5	+9.7	−8.5	−6.9	−8.2	+2.0	−5.6	+3.9	+5.2

Ions	*Thiourea* (*aq.*)	*Thiourea* (*pH 5.8*)	*Thiourea* (0.1N HCl)	*Anthranilic acid*	*Picolinic acid*	*Dimethylglyoxime* (0.1N $NaOH$)
Zn^{+2}	−4.0	−7.7	−4.0	0.0	−4.3	+1.4
Mn^{+2}	−1.5	−8.2	−2.5	0.0	−2.0	+1.7
Co^{+2}	−5.0	−7.7	−4.4	0.0	−3.0	+3.1
Ni^{+2}	−3.7	−6.2	−4.0	0.0	−0.6	0.0

TABLE II

MIGRATION SEQUENCES OF IONS PRESENT IN MIXTURES

Electrolytes	*Migration sequences*
HCl	:Zn,Co—; :Zn,Ni—
H_3PO_4	:Mn,Zn—; :Mn,Co—; :Mn,Ni—
KCl	:[Zn,Co]—; :[Mn,Co]—; :[Ni,Co]—
KI	:[Ni,Co], Mn—; :[Zn,Co], Mn—
$Na_2S_2O_3$	+Zn:Mn—; +Zn:Co—; +Zn:Ni—
NH_4CNS	:Zn,Mn—; :[Mn,Ni,Co]—
NH_4CNS(*N*)	+Mn,Zn:; +Mn,[Ni,Co]:
NaH_2PO_4(0.1*N* HCl)	:Mn,Zn—
NH_4OH(5*N*)	:Mn,[Zn,Ni]—; :Mn,Co,Ni—; :Mn,Co,Zn—
KCN(aq.)	+Ni,Co:Mn—; +Zn,Co:Mn—;
KCN + Br_2	+Ni,Co,Mn:; +Ni,Zn,Mn:
KCN(pH 6.0)	+Ni:Co,Mn—; +Ni:Zn,Mn—; +Ni:[Zn,Co],Mn—
Acetic acid	:Zn,Ni—; :[Zn,Mn]—; :[Zn,Co]—
NH_4 acetate	:Zn,Ni—; :Zn,Mn—; :[Zn,Co]—
Tartaric acid	:Zn,Co—; :Zn,[Ni,Mn]—
Na K tartrate	+[Ni,Zn]:Mn—; +[Co,Zn]:Mn—
Citric acid	:Zn,Mn—; :[Ni,Co], Mn—
Na citrate	+Co,Mn:; +Ni,Mn:; +Zn,Mn:
Thiourea(aq.)	:Mn,Zn—; :Mn,Co—; :Mn,Ni—
Thiourea (pH 5.8)	:Zn,Mn—; :Ni,Co—; :Ni,Mn—
Thiourea (0.1*N* HCl)	:Mn,Co—; :Mn,Ni—; :[Mn,Zn]—
Dimethylglyoxime (0.1*N* NaOH)	+Co,Ni:; +Mn,Ni:; +[Zn,Ni]:

potassium cyanide (aq.), ammonium thiocyanate (*N*) and dimethylglyoxime. With an increase in the concentration of ammonium thiocyanate, from 0.1*N* to *N*, the nature of the complexes changes from cationic to anionic; with the higher concentration of ammonia the cationic character and the migration rates of the ions increase, confirming the formation of ammine complexes. Both cobalt and nickel show two bands in sodium nitrite, and as both bands move towards the cathode, it may be assumed that they are due to the formation of simple and double nitrites.

SUMMARY

A study has been made of the electro-chromatographic separation of the ions of zinc, manganese, nickel and cobalt in the presence of a number of electrolytes. A few separations from mixtures of three ions have been achieved with the sequences Mn-Co-Ni, Ni-Co-Mn, Zn-Co-Mn and Mn-Co-Zn. A quaternary separation with ions in the sequence Ni-Zn-Co-Mn, with a slight spreading of the zinc band over that of cobalt, is possible only in the presence of a potassium cyanide solution maintained at a pH of 6.0.

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Received March 31st, 1958

DIRECT TITRATION OF FERRICYANIDE IN PRESENCE OF ZINC SULFATE

DETERMINATION OF NITRITE

by

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Methods of estimating nitrite are usually based upon its conversion to nitrate in acidic medium by a suitable oxidizing agent, and in practice the addition of an excess reagent followed by an iodometric titration of the excess is preferred[1]. While such reagents as permanganate, bromate, cerate, chloramine-T, iodine, and bromine have been recommended, it is well known that each of these methods is subject to rigid precautions owing to the tendency of nitrous acid to decomposition. Alkaline ferricyanide is a fairly powerful oxidizing agent and has been utilized for the analysis of hydroxylamine[2], thiocyanate[3], thiourea[4] and other reducing substances[5]. In the case of thiocyanate, the reaction takes place only in presence of osmic acid catalyst and cyanate and sulfate are the oxidation products. Preliminary experiments showed that ferricyanide, with or without osmic catalyst, is unable to oxidize nitrite ion in alkaline medium. However, in the presence of zinc sulfate the reaction proceeds quantitatively to nitrate. Depending upon this principle of the use of zinc sulfate, a titrimetric method for estimating hydrazine was reported recently from these laboratories[6]. The present paper describes an essentially similar procedure for the determination of nitrite.

EXPERIMENTAL

An aqueous solution of an accurately weighed Bakers' analyzed sodium or potassium nitrite was prepared and its nitrite content ascertained by the permanganate method[1]. Such nitrite solutions were found to be extremely stable for a period of four weeks. The potassium ferricyanide solution was standardized iodometrically against sodium thiosulfate.

To a known volume of ferricyanide solution taken in an Erlenmeyer flask or a china dish, 2–3 g pure zinc sulfate dissolved in about 15 ml water was added and the mixture heated to boiling. Nitrite solution was now run in from the buret until the complete decolorization of the solution marked the end-point.

$$2[\mathrm{Fe(CN)_6}]^{-3} + \mathrm{NO_2}^- + 2\ \mathrm{OH}^- \rightarrow 2[\mathrm{Fe(CN)_6}]^{-4} + \mathrm{NO_3}^- + \mathrm{H_2O}$$

$$2\mathrm{K_4}[\mathrm{Fe(CN)_6}] + 3\ \mathrm{ZnSO_4} \rightarrow \mathrm{K_2Zn_3}[\mathrm{Fe(CN)_6}]_2 + 3\ \mathrm{K_2SO_4}$$

Thus 1 ml 1 M $\mathrm{K_3}[\mathrm{Fe(CN)_6}]$ corresponds to 23 mg of $\mathrm{NO_2}^-$. A representative set of data is entered in Table I. It will be seen that the experimental values are in fair agreement with those obtained by the permanganate method.

DISCUSSION

Nitrous acid is susceptible to decomposition and therefore an inherent difficulty

TABLE I

DETERMINATION OF NITRITE BY FERRICYANIDE

$K_3[Fe(CN)_6]$ taken *M*	*ml*	$NaNO_2$ required *M*	*ml*	NO_2^- (mg) *Calcd.*	*Found*	*Diff.*
0.01980	5	0.00833	5.95	2.281	2.277	0.004
0.01980	10	0.00833	11.95	4.580	4.544	0.036
0.09901	5	0.0833	3.00	11.50	11.39	0.11
0.09901	10	0.0833	5.95	22.81	22.77	0.04
0.09901	15	0.0833	8.95	34.30	34.16	0.14
0.09901	20	0.0833	12.00	46.00	45.54	0.46

exists in the estimation of nitrite in acidic solutions. By oxidizing in an alkaline medium, this difficulty can be obviated.

$$NO_2^- + 2\,OH^- \rightleftarrows NO_3^- + H_2O + 2\,e \qquad E_B^\circ = -0.01 \text{ V}$$

However, nitrite ion is so stable in alkaline solutions that it is unattacked even by alkaline permanganate[1,7].

$$MnO_4^{-2} \rightleftarrows MnO_4^- + e \qquad E_B^\circ = -0.564 \text{ V}$$

The potential of the electrochemical reaction $[Fe(CN)_6]^{-4} \leftrightarrows [Fe(CN)_6]^{-3} + e$ in 0.01 *M* NaOH is given as —0.46 V[8]. In the present investigation advantage is taken of the rise in the oxidation potential of the ferricyanide ion through the removal of ferrocyanide as sparingly soluble zinc potassium ferrocyanide. Thus, the moment nitrite ion comes in contact with a mixture of potassium ferricyanide and zinc sulfate solutions (pH 6–7), it is oxidized rapidly to nitrate and the entire reaction is effected in an almost neutral medium. Further, the white zinc potassium ferrocyanide helps in the correct perception of the end-point. A series of experiments revealed that the titration can also be performed in a slightly alkaline solution provided the overall strength of sodium or potassium hydroxide does not exceed 0.3*N*. The accuracy of the method is not affected by the presence of a large quantity (ten times that of nitrite) of nitrate ion.

ACKNOWLEDGEMENT

The author is indebted to Dr. PHILIP W. WEST, Boyd Professor of Chemistry, for research facilities and encouragement.

SUMMARY

A rapid oxidimetric method for nitrite estimation, based upon the titration of ferricyanide in presence of zinc sulfate in aqueous or very slightly alkaline medium with a solution of sodium or potassium nitrite, is described. Complete decolorization of the solution marks the end-point. The presence of large quantities of nitrate causes no interference.

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Received March 24th, 1958

A COMPLEXOMETRIC TITRATION METHOD FOR DETERMINING CALCIUM IN THE PRESENCE OF MAGNESIUM

by

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Calcium and magnesium are nowadays usually determined by complexometric titration, for which various procedures have been suggested.

The most common method is to titrate calcium at pH > 12 where magnesium precipitates as hydroxide and to titrate the sum of calcium and magnesium at pH ≈ 10. Usually murexide is used as indicator for calcium, but several other indicators, *e.g.* Calcein[1], Calred[2], and Calcon[3], have also been suggested. Eriochrome Black T is an excellent indicator for titrating the sum.

However, the results are not quite satisfactory if considerable amounts of magnesium are present, since part of the calcium will coprecipitate with magnesium. Moreover, two separate titrations are needed, or murexide has to be destroyed before the second titration. The color change in titrating calcium is not quite satisfactory; particularly in artificial light a better contrast between the two colors would be desirable.

SCHWARZENBACH[4] has shown that the complexing agent ethyleneglycol-bis-aminoethylether-tetraacetic acid (Chel DE, Geigy), in the following abbreviated to EGTA (H_4X), forms a fairly stable complex with calcium, but a remarkably weak complex with magnesium. The stability constants are: $\log K_{CaX} = 11.0$ and $\log K_{MgX} = 5.4$. The difference between the two values is more than 5 logarithmic units, so this reagent seems very promising for the determination of calcium in the presence of magnesium. The difference in stability is quite sufficient for a stepwise titration, and errors caused by coprecipitation can thus be avoided.

However, the problem of detecting the end-point still remains to be solved. It is difficult to find a good calcium indicator at pH values where magnesium hydroxide does not precipitate, and Eriochrome Black T cannot be used as indicator for the sum since K_{MgX} is too small.

SCHMID AND REILLEY[5] have shown that a potentiometric method using a mercury electrode can be applied. However, it seems that a satisfactory method for the visual titration of calcium in the presence of magnesium is still lacking.

We now report the results of an investigation undertaken to solve this problem.

When searching for suitable indicators it is by no means necessary to look for a direct indicator. Often indirect indicators are quite as good. The best known example is the titration of calcium with EDTA (ethylenediaminetetraacetic acid) using Eriochrome Black T and a little of the Mg-EDTA complex (MgY) as indicator. Calcium reacts with EDTA before Mg since $K_{CaY} > K_{MgY}$, and the color change is sharp since $K_{\mathrm{MgI}} > K_{\mathrm{CaI}}$ (I = the indicator anion). K_{CaI} is too small for a sharp direct color change to be obtained.

We have tried to use a similar principle in titrating calcium with EGTA. In this titration we have to add a complex MX. The stability constant of this complex ought to be so large that a sudden change in pM takes place, but it should not be considerably larger than $K_{\mathrm{CaX}} = 10^{11.0}$.

The large difference between the stability constants of calcium and magnesium salts of EGTA shows that the size of the metal ion strongly influences the stability. Hence it is likely that there is a considerable difference between the constant of the cadmium complex and the constant of the zinc complex. For log K_{CdX} the value 16.73 has been reported by J. R. Geigy A.G. (personal communication), but we have found no value for K_{ZnX} in the literature.

Using the potentiometric method suggested by SCHMID AND REILLEY[6] and by SCHWARZENBACH AND ANDEREGG[7], we have determined this constant and found the value log $K_{\mathrm{ZnX}} = 12.8$ ($\mu = 0.1$). This value is much smaller than K_{CdX}, although it is still larger than log $K_{\mathrm{CaX}} = 11.0$.

However, more important than the true constant is the "apparent" constant introduced by SCHWARZENBACH[4] or — to use a term recently suggested by KOLTHOFF to one of the authors[8] — the *conditional constant* (since its value depends on the conditions). The conditional constant is defined by the equation

$$\frac{[\mathrm{MX}]}{[\mathrm{M'}]\,[\mathrm{X'}]} = K_{\mathrm{M'X'}} \quad \ldots\ldots\ldots\ldots \quad (1)$$

where [M′] denotes the sum of concentrations of all compounds containing M in some other form than MX, and [X′] denotes the sum of concentrations of all compounds containing X in other form than MX. In many analyses [M′] refers to the sum of ammonia complexes, and [X′] to the sum of proton complexes.

The conditional constants can be calculated from the α coefficients — in some connection they may be called "side-reaction coefficients" — defined by

$$\alpha_{\mathrm{M}} = \frac{[\mathrm{M'}]}{[\mathrm{M}]} \quad \ldots\ldots \quad (2) \qquad \alpha_{\mathrm{X}} = \frac{[\mathrm{X'}]}{[\mathrm{X}]} \quad \ldots\ldots \quad (3)$$

The relationship between the conditional constant and the true constant[4,8] is

$$K_{\mathrm{M'X'}} = \frac{K_{\mathrm{MX}}}{\alpha_{\mathrm{M}}\,\alpha_{\mathrm{X}}} \quad \ldots\ldots\ldots\ldots \quad (4)$$

If we wish to make the conditional constant of ZnX smaller, we can do this by increasing α_{Zn}, *i.e.* by binding zinc in some suitable zinc complexes. Ammonia is a good complexing agent, but it should be noted that zinc also forms rather strong hydroxo complexes.

If several agents compete in complexing the zinc ion, it can be assumed that the over-all side-reaction coefficient α_{Zn} is approximately equal to the sum of the individual side-reaction coefficients[8], *i.e.*

$$\alpha_{\mathrm{Zn}} \approx \alpha_{\mathrm{Zn(NH_3)}} + \alpha_{\mathrm{Zn(OH)}} \quad \ldots\ldots\ldots\ldots \quad (5)$$

Usually one of the individual side-reaction coefficients predominates and the others can be neglected.

For the calculation of the α values we have used the following equations:

$$\alpha_{\mathrm{Zn(NH_3)}} = 1 + \sum_{i=1}^{4} [\mathrm{NH_3}]^i \, K_{\mathrm{Zn(NH_3)}_i} \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

$\log K_1 = 2.27$; $\log K_2 = 4.61$; $\log K_3 = 7.01$; $\log K_4 = 9.06$ (according to BJERRUM[9]).

$$\alpha_{\mathrm{Zn(OH)}} = 1 + \sum_{i=1}^{4} [\mathrm{OH}]^i \, K_{\mathrm{Zn(OH)}_i} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

$\log K_1 = 4.4$; $\log K_2$ neglected; $\log K_3 = 14.4$; $\log K_4 = 15.5$ (according to FEITKNECHT[10])

$$\alpha_{\mathrm{X(H)}} = 1 + \sum_{j=1}^{4} [\mathrm{H}]^j \, K_{\mathrm{H}_j\mathrm{X}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

$\log K_1 = 9.43$; $\log K_2 = 18.28$; $\log K_3 = 20.96$; $\log K_4 = 22.96$ (according to SCHWARZENBACH[4])

To simplify the calculations, these equations are given in the form of graphs in Figs. 1 and 2.

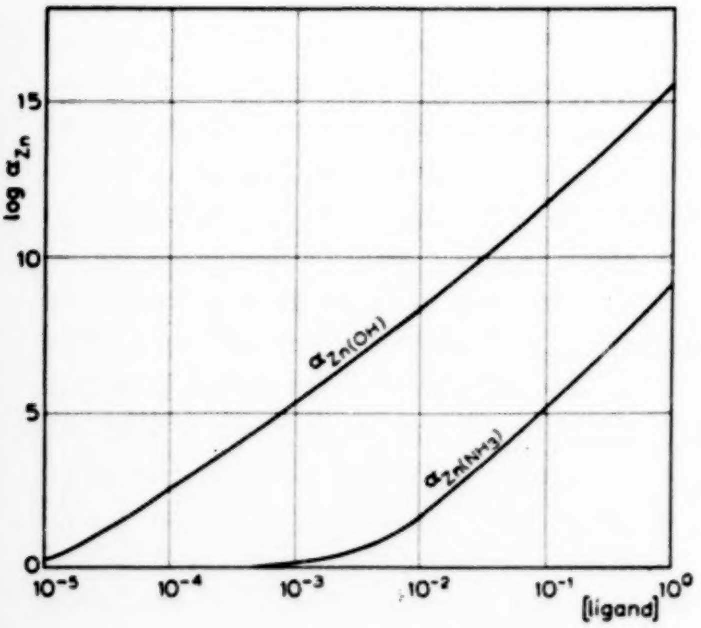

Fig. 1. $\alpha_{\mathrm{Zn(NH_3)}}$ and $\alpha_{\mathrm{Zn(OH)}}$ as functions of the ligand concentration.

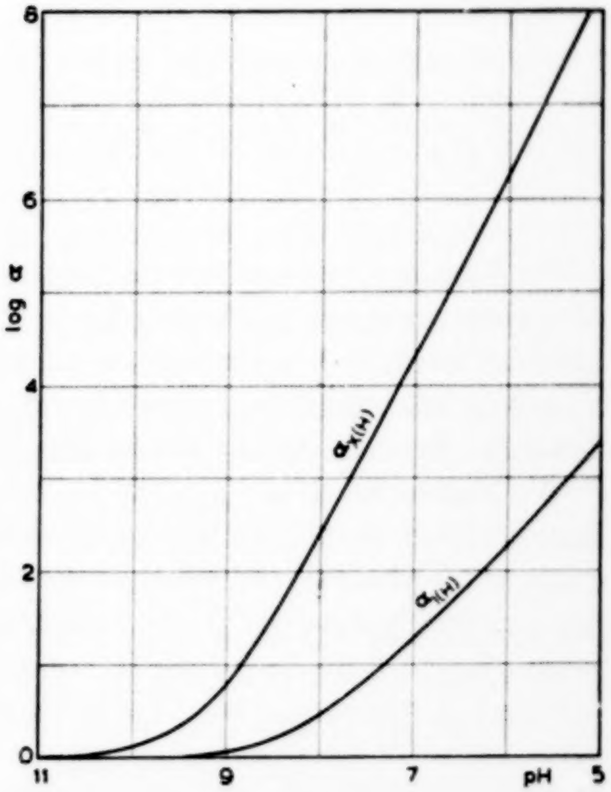

Fig. 2. $\alpha_{\mathrm{X(H)}}$ and $\alpha_{\mathrm{I(H)}}$ as functions of the hydrogen ion concentration.

By means of these curves and eqn. (4), the conditional equilibrium constants of the calcium, magnesium and zinc salts of EGTA have been calculated and are presented graphically as functions of pH in Fig. 3. The influence of ammonia on $K_{Zn'X'}$ is also shown.

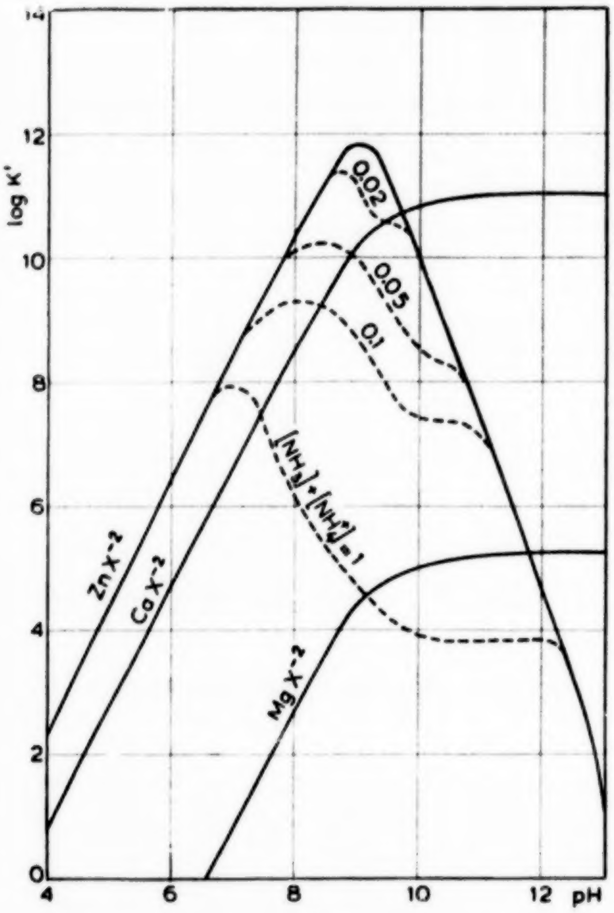

Fig. 3. Conditional constants of CaX, MgX and ZnX as functions of pH. log K_{CaX} = 11.0; log K_{MgX} = 5.4; log K_{ZnX} = 12.8.

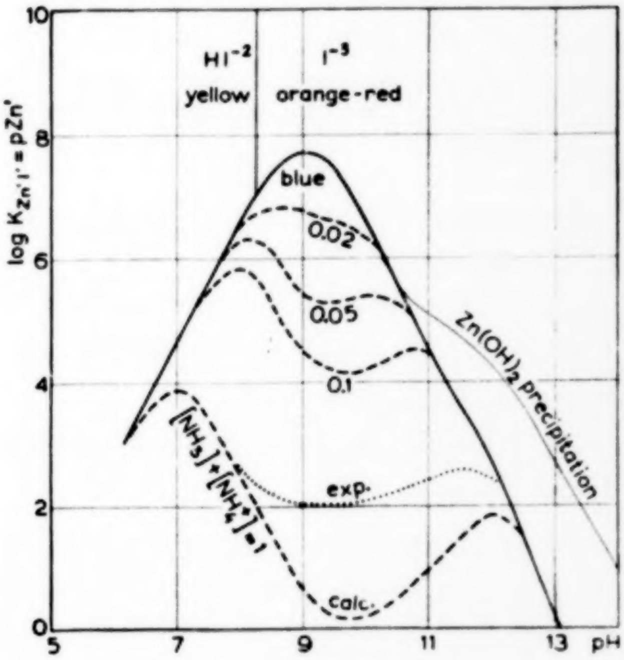

Fig. 4. Conditional constant of the zinc complex of Zincon as function of pH for various values of $[NH_3] + [NH_4^+]$.

The addition of ammonia does not affect $K_{CaX'}$ and $K_{MgX'}$. Since the formation of a basic complex ZnOHX is likely, the true conditional constant of ZnX in highly alkaline solution is probably a little larger than that obtained from Fig. 3.

Before the optimum experimental conditions for a titration can be defined, the indicator problem has to be discussed.

We have tried to use Zincon, *i.e.* 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene as indirect indicator. This substance was introduced by YOE AND RUSH[11] as a zinc reagent for photometric analysis. KINNUNEN AND MERIKANTO[12] showed that it is also an excellent indicator for the complexometric titration of zinc as it gives a brilliant color change from deep blue to orange-red. A particular advantage is that the color reaction is rather selective. Preliminary experiments with Zincon as an indirect calcium indicator were promising, and in order to be able to define suitable experimental conditions we determined the equilibrium constants of the indicator. This was done by spectrophotometric measurements. No details will be given here, only the results will be briefly summarized below.

References p. 531

The indicator is a tribasic acid, and the equilibria are

$$\underset{\text{red}}{H_3I} \longrightarrow \underset{\text{red-violet}}{H_2I^-} \xrightarrow{pK_2 = 4.5} \underset{\text{yellow}}{HI^{-2}} \xrightarrow{pK_3 = 8.25} \underset{\text{red-orange}}{I^{-3}}$$

$\alpha_{I(H)}$ calculated from eqn. (8) is presented graphically in Fig. 2.

The calculation of the stability constant of the zinc complex offered some difficulties. YOE AND RUSH have shown that a 1:1 complex is formed, but on assuming the formula ZnI, we did not obtain the relationship between pH and the conditional constant that should exist theoretically. However, when a complex compound ZnOHI was assumed, the agreement was fairly good. The constant was then approximately

$$\frac{[\text{ZnOHI}]}{[\text{ZnOH}]\,[\text{I}]} \approx 10^{8.6} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (8)$$

or, considering that $K_{\text{ZnOH}} = 10^{4.4}$

$$\frac{[\text{ZnOHI}]}{[\text{Zn}]\,[\text{I}]} \approx 10^{13.0}\,[\text{OH}] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (9)$$

Using the α values given in Figs. 1 and 2, $[\text{Zn}']$ and $[\text{I}']$ can be calculated (eqns. 2 and 3), and in Fig. 4 the conditional constant $[\text{ZnOHI}]/[\text{Zn}']\,[\text{I}']$ is plotted as a function of pH for various values of $[\text{NH}_3] + [\text{NH}_4]$. The logarithmic conditional constant is identical with pZn′ at the color transition point[8].

There was good agreement between calculated and experimental values except at high concentrations of ammonia where the experimental values were considerably larger, as can be seen from Fig. 4. The causes of this discrepancy will not be discussed here, possibly mixed ammonia-indicator complexes are formed.

From Figs. 3 and 4 it can be seen that a calcium titration with Zincon + ZnX as indicator gives the best results at pH values between 9.5 and 10. At pH = 10 no ammonia is needed, but at lower pH values a low concentration of ammonia (0.02–0.05M) is advantageous. In this range $K_{\text{Zn}'\text{X}'}$ is a little, but not too much, smaller than $K_{\text{Ca X}'}$. At very high concentrations of ammonia $K_{\text{Zn}'\text{X}'}$ and $K_{\text{Zn}'\text{I}'}$ are too small, *i.e.* the color changes are no longer sharp.

A few words may be said about the best ZnX concentration. The relationship between pCa and pZn′ in a solution containing the two metals is given by the equation

$$\text{pCa} = \text{pZn}' + \log \frac{K_{\text{CaX}'}}{K_{\text{Zn}'\text{X}'}} + \log \frac{[\text{ZnX}]}{[\text{CaX}]} \quad . \; . \; . \; . \; . \; . \; . \qquad (10)$$

obtained by combining the two stability constants. $K_{\text{CaX}'}$ is usually about one power of ten larger than $K_{\text{Zn}'\text{X}'}$ (Fig. 3). Consequently, if [ZnX] is about one-tenth of [CaX], pCa will be of the same order as pZn′. On the other hand, pCa_{eq} can be computed from the equation[8]

$$[\text{Ca}]_{\text{eq}} = \sqrt{\frac{[\text{CaX}]}{K_{\text{CaX}'}}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (11)$$

According to Fig. 3, log $K_{CaX'}$ is 10.5 to 11, and [CaX] in most titrations is 10^{-2} to 10^{-3}. Hence pCa_{eq} is 6 to 7. From Fig. 4 it can be seen that pZn′ at the color transition point is also about 6 to 7 in the pH range in question, provided the ammonia concentration is not high. A very sharp color change is therefore to be expected.

The following procedure is based on the theoretical considerations made above:

EXPERIMENTAL

Procedure

To 20–50 ml of the sample solution, add 20–50 ml of the buffer, 2 ml of 0.025*M* ZnX solution and 3 drops of the Zincon solution. The solution is titrated with 0.05*M* EGTA until the color changes from blue to clear orange-red.

The color change is very sharp. If large amounts of calcium are titrated, an increase of [ZnX] is favorable — [ZnX]/[CaX] must be about 1:10 — and attention has to be paid to the liberated hydrogen ions. pH should be kept at 9.5–10.

Solutions

0.05*M* EGTA solution (disodium salt): 19.01 g EGTA (acid) + 100 ml 1*N* NaOH are diluted to 1 l.

Buffer solution. pH ≈ 10: 25 g $Na_2B_4O_7 \cdot 10$ aq. + 3.5 g NH_4Cl + 5.7 g NaOH are dissolved in 1 l and kept in a plastic bottle.

Indicator solution. 65 mg Zincon + 2 ml 0.1*N* NaOH are diluted to 100 ml.

The ZnX solution is obtained by mixing equivalent amounts of 0.05*M* EGTA and 0.05*M* $ZnSO_4$.

The results of a few titrations are given in Table I.

The sum of calcium and magnesium can be determined with EDTA in a separate sample, using Eriochrome Black T as indicator. It is also possible to titrate magnesium in the solution used above for the determination of calcium, by continuing the titration with EDTA and using Eriochrome Black T as indicator. Dilution with hot water is advantageous here, and the color of Zincon does not interfere appreciably. However, this procedure presumes that [ZnX] is very small, since otherwise the following reactions will cause a disturbance:

$$\begin{aligned} ZnX + Y &\rightarrow ZnY + X \\ X + Mg &\rightarrow MgX \end{aligned}$$

TABLE I

DETERMINATION OF CALCIUM WITH EGTA

ml $CaCl_2$ $8.748 \cdot 10^{-2}M$	*ml* $MgSO_4$ $0.05M$	*ml* $4.951 \cdot 10^{-2}M$ Na_2H_2X	
		calc.	*found*
0.10	—	0.18	0.18
0.64	—	1.13	1.14
2.00	—	3.53	3.52
4.30	—	7.60	7.59
4.92	—	8.69	8.69
4.80	0.5	8.48	8.48
5.00	1.0	8.83	8.84
5.40	2.0	9.54	9.56
5.60	10.0	9.90	9.96

A correction can be made for the first reaction, but the second reaction is not complete and consequently the color change will not be sharp enough. If the concentration of calcium is low, ZnX can also be kept low, but with high calcium concentrations it is better to titrate the sum of calcium and magnesium with EDTA in a separate sample.

Finally, it may be mentioned that murexide can also serve as an indirect calcium indicator when titrating calcium with EGTA in the presence of a little ZnX. A brilliant color change from light yellow to red results. However, magnesium interferes with this color change, and, therefore, Zincon is preferred as indicator.

ACKNOWLEDGEMENTS

This investigation has been supported by grants from Statens Naturvetenskapliga Kommission, Finland. The authors wish to thank Geigy Co. Ltd., Switzerland, for placing samples of EGTA at their disposal.

SUMMARY

In the presence of magnesium, calcium can be titrated complexometrically with EGTA (ethyleneglycol-bis-aminoethylethertetraacetic acid = Geigy Chel DE = H_4X) using Zincon + ZnX as indirect indicator. The stability constants of the zinc complexes of EGTA and Zincon have been determined, and suitable experimental conditions have been suggested on the basis of theoretical considerations. The results of some titrations are presented.

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Received April 8th, 1958

SOLUBILITY OF *vic*-DIOXIMES IN UREA SOLUTIONS[*,**]

by

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INTRODUCTION

The *vic*-dioximes, especially 2,3-butanedione dioxime, commonly called dimethylglyoxime, are almost universally used as reagents for the detection and quantitative determination of nickel and palladium. Although these compounds fulfill almost all of the requirements for analytical reagents, low aqueous solubility is, in many cases, a serious drawback. In spite of their ability to dissolve the *vic*-dioximes more effectively than water, organic solvents are undesirable because of the danger of contaminating the precipitated bis(*vic*-dioximato-N,N')metal(II) complexes with the excess precipitant. Other attempts to increase the solubility of 2,3-butanedione dioxime using reagents such as sodium hydroxide, ammonium hydroxide and sodium peroxide have failed to produce stable aqueous solutions[1].

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[*] No. XXIII in a series on "Chemistry of the *vic*-dioximes". Previous paper in this series is No. XXII, *J. Am. Chem. Soc.*, in press.

[**] Contribution No. 618. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

In their studies to elucidate the structural properties of proteins, MIRSKY AND PAULING[2] reported the ability of urea and other hydrogen-bond-forming substances to denature proteins. These substances, it was explained, form hydrogen bonds with the protein side chains which are thus prevented from combining with one another.

The X-ray diffraction studies of MERRITT AND LANTERMAN[3] have shown that crystalline 2,3-butanedione dioxime consists of chains of essentially planar centrosymmetric 2,3-butanedione dioxime molecules joined together by a network of hydrogen bonds. The urea might be expected to have the same effect upon the hydrogen bonds of the 2,3-butanedione dioxime crystals as was observed for the proteins investigated by MIRSKY AND PAULING[2]. Consequently, the effectiveness of urea as a reagent for increasing the solubility of 2,3-butanedione dioxime and other *vic*-dioximes was studied. In addition to increasing the efficiency of the *vic*-dioximes now used as analytical reagents, it was thought that some of the more water-insoluble *vic*-dioximes might be rendered more useful.

SOLUBILITY OF THE *vic*-DIOXIMES IN UREA SOLUTION

The solubilities of 2,3-butanedione dioxime, 1,2-diaminoethanedione dioxime, 1,2-cyclohexanedione dioxime, 3,4-hexanedione dioxime, 3-methyl- and 4-methyl-1,2-cyclohexanedione dioxime, 1,2-cycloheptanedione dioxime, 4-isopropyl- and 4-*tert.*-amyl-1,2-cyclohexanedione dioxime and α-furil dioxime were determined in the presence of various concentrations of urea. Urea solutions were saturated with the various *vic*-dioximes at 25°, and aliquots of these saturated solutions were analyzed for *vic*-dioxime content. For the more soluble *vic*-dioximes it was found that the bis(*vic*-dioximato-N,N')nickel(II) complex would not precipitate quantitatively when an excess of nickel was present. The *vic*-dioxime content could, however, be determined spectrophotometrically. The *vic*-dioxime was precipitated with nickel(II), the bis(*vic*-dioximato-N,N')nickel(II) complex extracted into chloroform and the absorbancy measured at the appropriate wave length. The *vic*-dioxime content was determined by reference to a calibration curve. In the case of 1,2-diaminoethanedione dioxime, the absorbancy maximum of the *vic*-dioxime group was measured at 232 mμ. The solubility was determined by reference to a calibation curve. The solubilities of 3,4-hexanedione dioxime and α-furil dioxime were determined gravimetrically following precipitation of the bis(*vic*-dioximato-N,N')nickel(II) complex.

With the exceptions of α-furil dioxime and 1,2-cyclohexanedione dioxime, all of the above *vic*-dioximes exhibited increased solubility with increasing urea concentration. Solubility data for several *vic*-dioximes are summarized in Table I.

In some instances, the increase in solubility was very pronounced. Solubility factors, *i.e.*, the ratio of the solubility in 50% urea to the aqueous solubility, for several *vic*-dioximes are listed in Table II.

Although the equilibration of 1,2-cyclohexanedione dioxime in urea solution resulted in compound formation, the solubility of several of its alkyl-substituted derivatives was appreciably increased. The effect of urea on the solubility of the *vic*-dioximes was most pronounced in the cases where bulky substituent groups were present. Solubility curves for 1,2-cyclohexanedione dioxime and some of its alkyl-substituted derivatives are shown in Fig. 1.

Fig. 2 shows solubility curves for 1,2-cyclohexanedione dioxime and its next higher homologue, 1,2-cycloheptanedione dioxime, as a function of the urea concentration. While increasing the urea concentration promoted compound formation in the case of 1,2-cyclohexanedione dioxime, the solubility of 1,2-cycloheptanedione dioxime increased rapidly.

TABLE I

MOLAR SOLUBILITY OF SEVERAL *vic*-DIOXIMES IN UREA SOLUTIONS

vic-Dioxime	*Molar solubility at 25°*					
	Urea concentration (weight %)					
	0	*10*	*20*	*30*	*40*	*50*
2,3-Butanedione dioxime	0.0055	0.0073	0.0085	0.0108	0.0129	0.0152
1,2-Diaminoethanedione dioxime	0.1670	0.2305	0.2950	0.3774	0.4542	0.5497
1,2-Cyclohexanedione dioxime	0.064	0.086	0.026	0.016	0.012	0.008
3,4-Hexanedione dioxime	0.0028	0.0034	0.0054	0.0085	0.0134	0.0200
3-Methyl-1,2-cyclohexanedione dioxime	0.074	0.102	0.134	0.176	0.235	0.316
4-Methyl-1,2-cyclohexanedione dioxime	0.032	0.042	0.057	0.075	0.104	0.141
1,2-Cycloheptanedione dioxime	0.0376	0.0574	0.0815	0.1135	0.1580	0.2130
4-Isopropyl-1,2-cyclohexanedione dioxime	0.0064	0.0084	0.0140	0.0208	0.0285	0.0396
4-*tert*.-Amyl-1,2-cyclohexanedione dioxime	0.00016	0.0004	0.0007	0.0011	0.0016	0.0024
α-Furil dioxime[a]	0.0033					

[a] No solubility data here due to compound formation.

TABLE II

PHYSICAL PROPERTIES OF SOME *vic*-DIOXIMES

vic-Dioxime	*M.P. °C*	*M.W.*	*H-Bonding absorption maximum μ*	*Aqueous molar solubility at 25°*	*Sol. factor*[a]
2,3-Butanedione dioxime	240	116	3.11	0.0055	2.76
1,2-Diaminoethanedione dioxime	200	118	2.97	0.1670	3.22
1,2-Cyclohexanedione dioxime	199	142	2.95	0.064	—
3,4-Hexanedione dioxime	186	144	3.12	0.0028	7.14
3-Methyl-1,2-cyclohexanedione dioxime	166	156	3.02	0.074	4.27
4-Methyl-1,2-cyclohexanedione dioxime	193	156	2.94	0.032	4.41
1,2-Cycloheptanedione dioxime	179	156	3.05	0.0376	5.66
4-Isopropyl-1,2-cyclohexanedione dioxime	184	184	2.91	0.0064	6.19
4-*tert*.-Amyl-1,2-cyclohexanedione dioxime	202	212	2.92	0.00016	15.00

[a] The solubility factor is the ratio of the solubility of the *vic*-dioxime in 50% urea solution to the aqueous solubility.

Solubility curves for 2,3-butanedione dioxime and 3,4-hexanedione dioxime, Fig. 3, illustrate the difference in the ability of urea to affect the solubility of these *vic*-dioximes. It is observed that the solubility curve for 2,3-butanedione dioxime rises gradually; in comparison, the solubility curve for 3,4-hexanedione dioxime rises rapidly. The difference in the effect of the urea on the solubilities of these two *vic*-dioximes is, as is seen from a comparison of their physical properties in Table II, related to the total intermolecular forces, *e.g.*, 2,3-butanedione dioxime melts at 240°, while 3,4-hexanedione dioxime melts at 186°. The infrared absorption maxima for associated hydrogen

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bonding occur at similar wave lengths and indicate that the strength of the hydrogen bonding is not the primary factor determining the solubility. In the absence of urea, the difference in the solubilities of 2,3-butanedione dioxime and 3,4-hexanedione dioxime is probably due to the difference in their molecular weights. The effect of molecular weight, however, appears to become less important as the urea concentration is increased. The solubility of the more insoluble 3,4-hexanedione dioxime increases with increasing urea concentration until its solubility surpasses that of 2,3-butanedione dioxime in 50% urea solution.

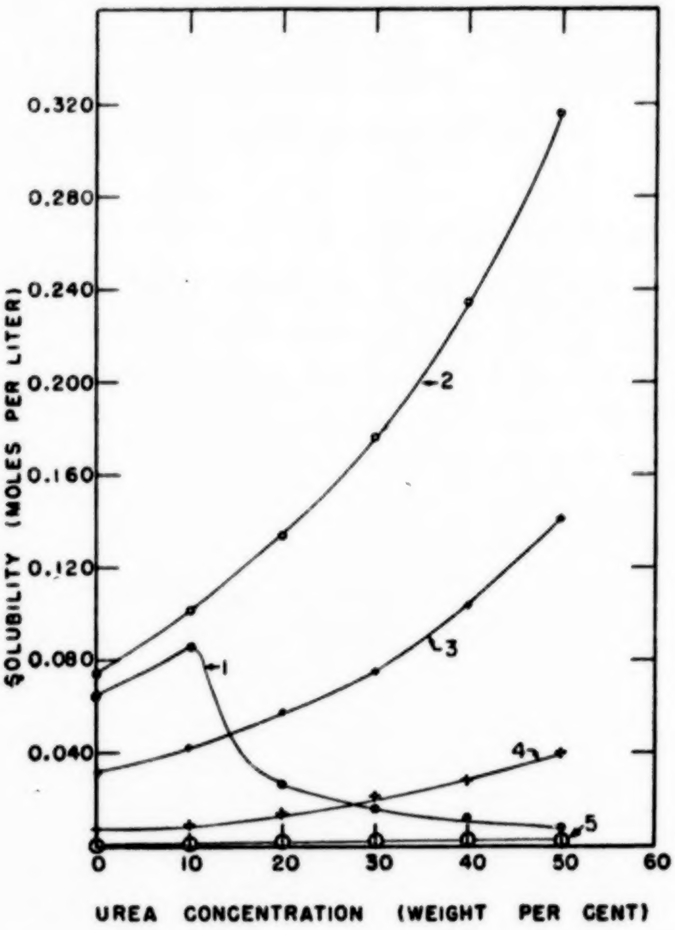


Fig. 1. Solubilities of 1,2-cyclohexanedione dioxime and some of its alkyl-substituted derivatives in urea solutions at 25°. 1. 1,2-Cyclohexanedione dioxime; 2. 3-Methyl-1,2-cyclohexanedione dioxime; 3. 4-Methyl-1,2-cyclohexanedione dioxime; 4. 4-Isopropyl-1,2-cyclohexanedione dioxime; 5. 4-*tert.*-Amyl-1,2-cyclohexanedione dioxime.

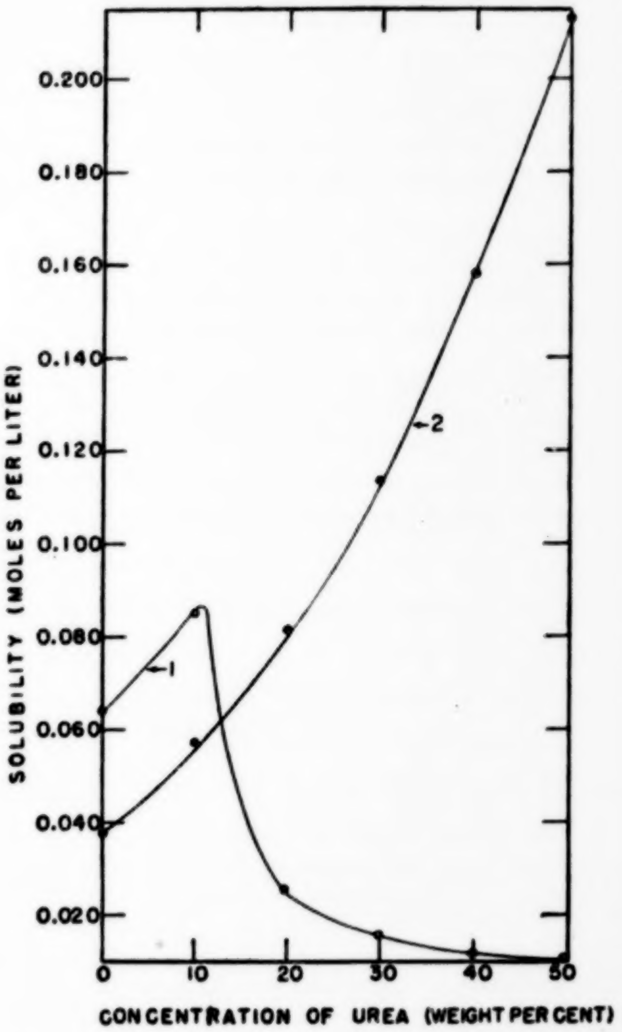


Fig. 2. Solubilities of 1,2-cyclohexanedione dioxime (1) and 1,2-cycloheptanedione dioxime (2) in urea solutions at 25°.

1,2-Diaminoethanedione dioxime contains two amino groups which probably contribute significantly to intermolecular hydrogen bonding. Therefore, it is not surprising that the solubility of this *vic*-dioxime is not greatly increased by urea. Its solubility curve, Fig. 4, rises gradually as the urea concentration is increased.

Because the urea has to break intermolecular hydrogen bonds in dissolving the *vic*-dioximes, it would appear that its effect on solubility would be greater in cases when the intermolecular association is weak. While the effect of the urea on the solubility of the *vic*-dioximes is believed to be influenced by the strength of the intermolecular hydrogen bonding in these compounds, a tabulation of the infrared absorption maximum for associated hydrogen bonding and other physical properties for the several *vic*-dioximes indicates that other factors quite often predominantly affect the solubility.

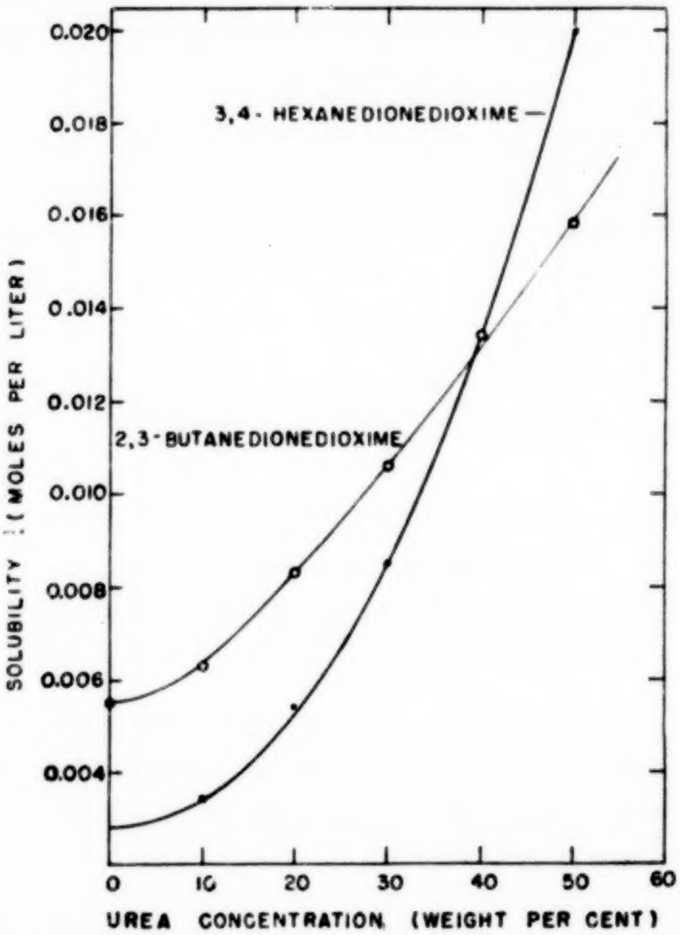


Fig. 3. Solubilities of 2,3-butanedione dioxime and 3,4-hexanedione dioxime in urea solutions at 25°.

The hydrogen bonding absorption maxima listed in Table II were obtained from spectra prepared on the Perkin-Elmer, Model 13, infrared spectrophotometer. This instrument, equipped with lithium chloride optics, gives high resolution in the wave length range from 2–5 μ.

3-Methyl- and 4-methyl-1,2-cyclohexanedione dioxime are of special interest because they were the only isomeric pair studied. The 3-methyl-1,2-cyclohexanedione dioxime crystallizes in a powdery form which melts at 166°, whereas the 4-methyl-1,2-cyclohexanedione dioxime melts 27° higher, at 193°, and crystallizes in the form of needles. This difference in melting point would indicate that there is a marked difference in the intermolecular forces in the crystals. This difference is also borne out in the solubility data which show 3-methyl-1,2-cyclohexanedione dioxime to be more than twice as soluble in water and in the various urea solutions investigated as is 4-methyl-1,2-cyclohexanedione dioxime. Evidently hydrogen bonding has little affect on the solubility of these two compounds because their infrared spectra show that the former contains stronger intermolecular hydrogen bonds than the latter.

The equilibration of α-furil dioxime in urea solutions resulted in the formation of 3,4-bis-(2-furyl)-1,2,5-oxadiazole which was originally obtained as a product of the pyrolysis of bis(α-furil dioximato-N,N′)nickel(II) and characterized by TSUMAKI AND

YAMAGUCHI[4]. The procedure for preparing this compound in 58% yield by heating α-furil dioxime in 50% urea solution has been described by BANKS AND ADAMS[5].

The equilibration of 1,2-cyclohexanedione dioxime, commonly called nioxime, in urea solutions also resulted in compound formation. The compound obtained in this case was characterized as a monohydrated two to one urea to 1,2-cyclohexanedione dioxime complex which has been referred to, for convenience, as the "urea-nioxime complex". Because of its analytical interest, its preparation, properties, characterization and applications are described.

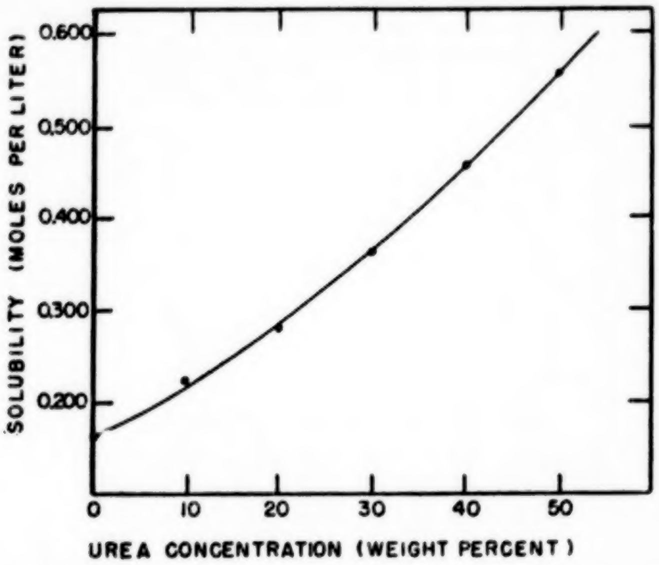


Fig. 4. Solubility of 1,2-diaminoethanedione dioxime in urea solutions at 25°.

UREA-NIOXIME COMPLEX

Preparation

The urea-nioxime complex is readily prepared by a method described by TRUTER[6] for the preparation of urea adducts of aliphatic hydrocarbons. One part of a saturated ethanolic or methanolic solution of 1,2-cyclohexanedione dioxime is added, with swirling, to two parts of a saturated aqueous urea solution. When methanol is used as the solvent for 1,2-cyclohexanedione dioxime, crystallization of the product is instantaneous, and the crystals are very small. When the *vic*-dioxime is dissolved in ethanol, crystallization begins within 20 to 30 min after the solutions are mixed and proceeds slowly, giving large, well-formed crystals. In either case, the reaction mixture is allowed to stand for 2-3 h to assure complete precipitation of the product. The crystals are filtered and air-dried. They are brought to constant weight by drying in a desiccator over anhydrous phosphorus pentoxide or by drying in an oven at 80° for 2 h.

Chemical properties

The urea-nioxime complex breaks down in dilute aqueous solution to give its constituent compounds. Bis(1,2-cyclohexanedione dioximato-N,N')nickel(II) is readily precipitated from aqueous and alcoholic solutions of the urea-nioxime complex.

Physical properties

The urea-nioxime complex, a white crystalline solid with a molecular weight of 280.29, melts at 116-117°. By precipitating the 1,2-cyclohexanedione dioxime from aliquots of a saturated solution of the urea-nioxime complex with excess nickel(II), the solubility of the urea-nioxime complex was found to be 18.78 g (0.067 mole) per l at 25°. The density of the urea-nioxime complex, as determined by the volumes of nitrobenzene and 1,2-dichlorobenzene displaced by known weights of the compound, is 1.369 g per ml. X-ray diffraction studies, using single-crystal methods, revealed that the crystals of the urea-nioxime complex are triclinic with the lattice constants a = 14.0 Å, b = 19.5 Å and c = 8.6 Å. The unit cell contains seven molecules.

Characterization

Elemental analyses were carried out on samples of the urea-nioxime complex; carbon and hydrogen were determined by microcombustion methods[7], nitrogen analyses were carried out according to the Kjeldahl procedure and the oxygen content was found by difference. For $C_8H_{20}N_6O_5$:

	% C	% H	% N	% O
Calculated	34.28	7.19	29.99	28.54
Found	34.57	7.29	29.60	28.53

The carbon to nitrogen ratio for $C_8H_{20}N_6O_5$: Calculated 1.14, Found 1.17.

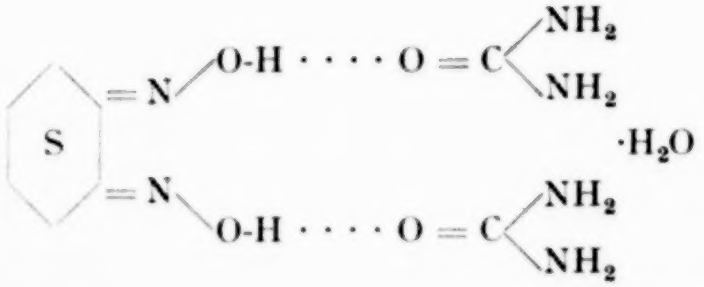
Colorimetric determinations of urea, using diacetyl monoxime as the reagent, according to the method of ORMSBY[8] gave a molar ratio of urea to 1,2-cyclohexanedione dioxime of two.

Karl Fischer titrations on samples of the complex, oven-dried to constant weight, indicated the presence of one mole of water of hydration per mole of complex.

On the basis of these findings the following configuration was assigned the new compound:

$$C_6H_{10}N_2O_2 \cdot 2CO(NH_2)_2 \cdot H_2O$$

A comparison of the infrared spectrum of the urea-nioxime complex with the spectra of urea and 1,2-cyclohexanedione dioxime revealed that the new compound retains many of the characteristics of 1,2-cyclohexanedione dioxime along with absorption maxima due to the presence of the urea. Absorption due to intermolecular association, however, occurred at 2.94 μ, a position different from that due to intermolecular association in either of the constituent compounds. This tends to suggest the formation of new hydrogen bonds due to an interaction between urea and 1,2-cyclohexanedione dioxime, making the following configuration seem plausible:



Analytical applications

BICKERDIKE AND WILLARD[9] reported the quantitative precipitation of nickel(II) from homogeneous solution using a 1% propanolic solution of 2,3-butanedione dioxime

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and urea. Under these conditions, quantities of nickel(II) up to 100 mg were successfully determined.

Experiments involving the analysis of aliquots of standard nickel solutions indicated that the urea–nioxime complex, in the presence of additional urea, may be used as a reagent for the quantitative precipitation of nickel from homogeneous solution. A procedure for its use in this capacity is described.

Reagents

Hydrochloric acid, C. P., specific gravity 1.19.

Nickel(II) chloride solution. Approximately 8.106 g of special reagent grade (low in cobalt) nickel (II) chloride 6-hydrate (J. T. Baker Chemical Co., Phillipsburg, N. J.) are dissolved in water and diluted to 200 ml. The solution is standardized by precipitating the nickel as bis(1,2-cycloheptanedione dioximato-N,N')nickel(II).

Solution of urea–nioxime complex, 0.067*M*. A saturated aqueous solution of the urea–nioxime complex is prepared.

Urea. Reagent grade, crystal (J. T. Baker Chemical Co., Phillipsburg, N. J.).

Recommended procedure

Samples containing up to 20 mg of nickel are diluted to 100 ml with deionized water. Sample solutions are adjusted to pH 1 by the addition of conc. HCl. 40 g of urea are added and dissolved. 10 ml of the saturated solution of the urea–nioxime complex, per 10-mg quantity of nickel, are added, and the samples are heated to 80°. The sample solutions, being stirred occasionally, are allowed to remain at this temperature for 20 min. Digestion is continued at 60° for 20 min. Then the precipitates are collected in weighed glass-filter crucibles of medium porosity, washed with five 20-ml portions of hot water and dried for 1 h at 110°. The factor for nickel is 0.1721.

TABLE III

DETERMINATION OF NICKEL

Ni taken g	*Weight of precipitate* g	*Average Ni found* g	*Error* mg
0.00910	0.05271	0.00907	−0.03
0.02008	0.11671	0.02010	+0.02
0.03000[a]	0.17396	0.02994	−0.06
0.04064[b]	0.23567	0.04057	−0.07

[a] Volume, 125 ml; initial pH, 0.8; digested at 80° for 15 min.
[b] Volume, 125 ml; initial pH, 0.6; digested at 80° for 15 min.

RESULTS AND DISCUSSION

Table III shows the results of analyses using the urea–nioxime complex as the reagent. Quantitative results were readily obtained for samples containing 10 and 20 mg quantities of nickel. However, the procedure as described yielded high results for samples containing 30 and 40 mg of nickel. In these cases, the final pH of the samples usually ranged from 5–7 compared to the desired pH range of 4–5. It appeared that coprecipitation of excess reagent was favored by high pH conditions. Hence, further adjustment of initial pH and digestion conditions was required for the quantitative precipitation of larger quantities of nickel.

The use of the urea–nioxime complex as a reagent for the determination of nickel offers the following advantages over the use of 1,2-cyclohexanedione dioxime by the method described in the literature[10]:

1. The solubility of 1,2-cyclohexanedione dioxime is increased by a factor of 1.2.

2. The precipitation of bis(1,2-cyclohexanedione dioximato-N,N')nickel(II) proceeds, in the presence of additional urea, from homogeneous solution.

3. The precipitates are more dense and, hence, more easily filtered than those usually obtained with 1,2-cyclohexanedione dioxime. Filterability has often been a serious drawback in the use of 1,2-cyclohexanedione dioxime as a reagent for nickel. Often, as long as 2.5 h were required for filtering a precipitate containing 15 mg of nickel. Using the present procedure, the filtration process, due to the nature of the precipitate, is greatly accelerated as is shown by the data below:

Wt. of Ni *mg*	*Wt. of precipitate* *g*	*Filtering time* *min*
10	0.05811	4–5
20	0.11612	12
30	0.17463	19
40	0.23773	23

Filtering time includes the thorough washing of the precipitates.

4. The use of a nioxime factor in the calculations is eliminated. The factor for nickel is the theoretical value, 0.1721.

ACKNOWLEDGEMENTS

The authors wish to thank R. E. RUNDLE and DENNIS W. BARNUM for the crystallographic information on the urea–nioxime complex.

The authors are also grateful to ROBERT McCORD and ROBERT KROSS for their help with the infrared spectra of the urea–nioxime complex and its constituents.

SUMMARY

The solubilities of 2,3-butanedione dioxime, 1,2-diaminoethanedione dioxime, 1,2-cyclohexanedione dioxime, 3,4-hexanedione dioxime, 3-methyl- and 4-methyl-1,2-cyclohexanedione dioxime, 1,2-cycloheptanedione dioxime, 4-isopropyl- and 4-*tert*.-amyl-1,2-cyclohexanedione dioxime and α-furil dioxime were determined as functions of the urea concentration in aqueous solutions at 25°. With two exceptions, all of the above *vic*-dioximes exhibited increased solubility with increasing urea concentration. In the presence of urea, α-furil dioxime undergoes catalytic dehydration to form 3,4-bis-(2-furyl)-1,2,5-oxadiazole. 1,2-Cyclohexanedione dioxime forms a sparingly soluble compound with urea which has been characterized as a monohydrated two to one urea to 1,2-cyclohexanedione dioxime complex and has been found to have interesting analytical applications.

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Received April 8th, 1958

COMPLEXOMETRIC TITRATION OF GALLIUM WITH FLUORESCENT INDICATOR

by

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The formation of gallium 8-hydroxyquinolate and its fluorimetric determination has been reported by several authors[1-4].

In all of these the authors determine gallium after extracting the complex into chloroform, and measuring the fluorescence.

It is well known that EDTA (ethylenediamine tetracetic acid) forms a stable complex with gallium, and several papers have been published describing a complexometric titration. MILNER[5] titrated gallium with EDTA at pH 2.8 using gallocyanine as indicator. PATROVSKY[6] used morin as a fluorescence indicator in acetic acid medium, while FLASHKA AND ABDINE[7] added excess EDTA and back titrated with standard zinc or lead solutions, using Eriochrome Black T or other indicators.

None of these methods are entirely specific, so that a preliminary separation of gallium is normally desirable. The simplest method is that described by MILNER, WOOD AND WOODHEAD[8] where gallium is extracted by diethylether (methyl ethyl ketone can also be used) from a mixed sulphuric acid–ammonium chloride solution. After extraction, gallium is returned to the aqueous phase by back-extraction with water, and the solution can be evaporated to low bulk, but not to dryness, without losing any gallium.

On examination of the above methods of determination, various disadvantages became evident. The gallium hydroxyquinolate fluorescence method was[1-4] found to be very sensitive but not very accurate for quantities of gallium greater than about 10 μg. The EDTA titration method, with gallocyanine indicator[5] gave a good end-point when $0.02M$ EDTA was used for > 2 mg gallium, but a rather indistinct end-point when the $0.002M$ EDTA solution was used.

The method using EDTA and morin as indicator[6] also gave a rather indefinite end-point, as in our experience there was considerable background fluorescence after the end-point had been reached. The back titration method[7] also gave a rather indistinct end-point when $0.001M$ EDTA solutions were used.

The possibility of titrating gallium with EDTA was investigated, using 8-hydroxyquinoline as a fluorescent indicator. The titration was carried out in near darkness, with a Hanovia fluorescence lamp as U.V. source. It was found that the end-point was very sharp ($\pm$ 0.1 ml using $0.001M$ EDTA solution in a total volume of about 20 ml). The decomposition of the gallium hydroxyquinolate by the EDTA was rapid, in absence of alcohol and chloroform. (Alcohol quenched the fluorescence while chloroform made it impossible to reach an end-point.) When excess EDTA was added, there was a very faint residual fluorescence. A solution previously titrated was therefore retained for comparison purposes. It is necessary to control the pH between about 2.5 and 3.5, and the phthalate buffer described by SANDELL[4] was found to be admirable. Using this method, it was possible to determine gallium in the range 50-1000 μg with reasonable accuracy, as Table I illustrates. Below 50 μg high titrations are found, using the conditions described. More accurate titrations can be obtained if a lower concentration of 8-hydroxyquinoline is used, but the end-point is rather uncertain.

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TABLE I

Gallium added μg	*Gallium found* μg	*Subtract indicator blank* μg	*Error* %
nil	5	—	—
20	42	37	+85
50	56	51	+ 2
100	108	103	+ 3
200	206	201	+ 0.5
300	310	304	+ 1.3
500	498	493	— 1.4
800	787	782	— 2.2
1000	1010	1005	+ 0.5
20[a]	28	23	+15

[a] Only two drops hydroxyquinoline indicator.

PROCEDURE

Evaporate a solution containing gallium (for example that obtained after extraction of gallium by ether from sulphate-chloride solution[8] and back extraction with water), to about 5 ml*. Add 5 ml 4% potassium hydrogen phthalate solution, and add 10% potassium hydroxide (if necessary) to bring the pH within the range 2.5-3.5. Add 1 ml 20% hydroxylamine hydrochloride solution and 1 ml 0.05% hydroxyquinoline** in 0.5% acetic acid. Titrate, using a U.V. lamp in near darkness, with 0.001 *M* EDTA, adding this slowly as the fluorescence fades, until the end-point is reached. This is best observed by comparing with a previous titrated gallium solution.

1 ml 0.001 *M* EDTA = 69.7 μg gallium.

SUMMARY

A method for titrating gallium with EDTA, using 8-hydroxyquinoline as fluorescent indicator is described, suitable for 50-1000 μg gallium.

ACKNOWLEDGEMENT

The author wishes to express appreciation to his colleagues in the B.T-H Research Laboratory for their interest in this work.

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Received April 29th, 1958

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* Avoid boiling strong hydrochloric acid solutions, as gallium may be lost.

** It is necessary, with very low gallium contents, to subtract the indicator blank, usually about 0.1 ml. Below 50 μg gallium, use only 2 drops of hydroxyquinoline solution.

T-5415

MICRODOSAGE COLORIMÉTRIQUE DES THIOLS EN MILIEU ALCOOLIQUE PAR LA N-ÉTHYL-MALÉIMIDE*

par

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INTRODUCTION

Depuis les études fondamentales de **Friedmann** *et al.*[1-3] sur les inhibiteurs de la mitose, la N-éthyl-maléimide est devenue un réactif courant, spécifique et rapide des groupes thiolés.

Friedmann a montré[4] que le comportement spectral de cette substance dans l'U.V. ne suit pas la loi de Beer (dans la région 205–240 mμ), ce qui rend son utilisation peu aisée pour doser les thiols par ce type de photométrie. **Gregory**[5] montre cependant que l'extinction des carbonyles, à 302 mμ ($e_M = 620$), disparaît lorsque la maléimide réagit avec un thiol. Cette variation d'extinction est vraisemblablement due à la rupture de la double liaison centrale, et, par conséquent, à la disparition de la conjugaison: les deux groupes $C=O$ ne présentent plus qu'une extinction molaire de quelques dizaines d'unités. Cette modification spectrale, utilisable en milieu neutre ou légèrement acide (pH 5 à 7), est cependant 12 fois moins sensible que celle obtenue par action du *p*-chloromercuribenzoate sur les thiols[6].

Tsao et Bailey[7] ont utilisé analytiquement la N-éthyl-maléimide pour titrer les thiols avec le nitroprussiate comme indicateur. Cette méthode permet la détermination de quantités de l'ordre de 0.1 mg de cystéine (ou 10 mg de protéine à 1% de -SH), soit 10^{-6} mole, avec une précision de 5%.

La méthode décrite ci-dessous permet le dosage colorimétrique direct des thiols sur 10^{-8} à 10^{-7} mole. Elle est basée sur la découverte, par **Benesch** *et al.*[8], d'un complexe coloré apparaissant lors de l'alcalinisation du produit de la réaction d'un thiol sur la N-éthyl-maléimide en milieu alcoolique.

RÉSULTATS EXPÉRIMENTAUX

Les conditions décrites par **Benesch** *et al.*[8] pour la détection des thiols ne permettent pas d'application quantitative directe. En effet, le solvant étant un alcool (isopropanol absolu), il y a lieu de tenir compte, avant tout, de la réaction compétitive de l'alcool sur la maléimide[9]. D'autre part, le maximum de coloration n'est obtenu qu'avec un très grand excès de réactif (10^3 à 10^4) qui conditionne, comme on le verra plus loin, la quantité d'agent alcalinisant à utiliser. Enfin, la substance colorée n'est stable que dans des conditions bien déterminées.

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* Ce travail a été subsidié par l'I.R.S.I.A. (Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture) et par le Comité Belge pour l'Etude des Froments Indigènes et leur Amélioration.

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Dans les expériences qui suivent, tous les réactifs étaient en solution dans l'isopropanol.

Effet du solvant

Dans un tube, on introduit 0.2 ml de N-éthyl-maléimide $5 \cdot 10^{-2} M$ et 0.2 ml de β-mercapto-éthanol $10^{-3} M$. On laisse réagir 5 min, puis on ajoute 0.2 ml d'hydroxyde de potassium $N/40$. On dilue immédiatement avec 5 ml d'un des solvants mentionnés, et on suit la variation de la coloration à 515 mμ, en fonction du temps. Dans le Tableau I sont consignés les résultats obtenus avec 17 solvants. On peut en conclure, conformément aux observations de BENESCH *et al.*[8], que la réaction n'est intéressante que dans certains alcools (éthanol, isopropanol, éthanolamine, et, à un moindre degré, l'éthylène-glycol). On voit également que la constante diélectrique du solvant semble sans influence sur la réaction.

TABLEAU I

VARIATION DE L'INTENSITÉ DE COLORATION DONNÉE, À 515 mμ, PAR 0.2 ml DE β-MERCAPTO-ÉTHANOL $10^{-3} M$, 0.2 ml DE N-ÉTHYL-MALÉIMIDE $5 \cdot 10^{-2} M$ ET 0.2 ml DE KOH $N/40$, AUXQUELS ON AJOUTE 5 ml DE SOLVANT. LE TEMPS EST COMPTÉ À PARTIR DE L'INTRODUCTION DE L'HYDROXYDE

Temps: sec	*30*	*45*	*60*	*90*	*120*	*150*	*180*	*15 min*	*Solvant*	*Constante diélectrique*
	—	585	595	597	599	600	602	601	isopropanol	14
	480	400	383	366	348	332	320	240	eau	80
	610	608	605	595	588	580	574	410	acétone	21
	—	539	536	490	420	381	371	180	chloroforme	5
	280	255	231	204	188	—	—	12	éther diéthylique	4
	incolore								formamide	
	incolore								N,N-diméthyl-formamide	
	—	297	303	302	302	305	312	303	éthylène-glycol	41
	—	475	470	465	460	455	450	415	méthoxy-éthanol	
	incolore								dioxane	2
	—	—	435	421	417	390	383	326	méthanol	31
	—	—	555	573	579	584	585	575	éthanolamine	
	—	510	510	500	492	488	480	268	cyclohexane	2
	515	504	504	478	453	450	455	204	tétrachlorure de carbone	2
	incolore								éther di-isopropylique	
	incolore								acétate d'éthyle	6
	—	590	590	593	596	600	604	599	éthanol	25

Les intensités de la coloration sont indiquées en millièmes de densité optique.

Effet de l'agent alcalinisant

Si, dans les conditions décrites ci-dessus, on fait varier la quantité d'hydroxyde de potassium, on remarque qu'il peut être un facteur limitant dans le développement de la coloration (Fig. 1), mais qu'il tend également à détruire le composé coloré lorsque sa concentration s'élève (Fig. 2). Ainsi que BENESCH *et al.*[8] l'ont fait remarquer, la réaction préalable de la maléimide sur l'hydroxyde ne permet plus la réaction avec les thiols. On peut donc admettre que l'excès d'hydroxyde introduit est consommé pour la destruction de la maléimide, elle aussi en excès par rapport au thiol. GREGORY[5] a d'ailleurs montré qu'en milieu aqueux, la maléimide est rapidement détruite dès que le pH s'élève au-dessus de 7. Notons également, avec BENESCH, que l'introduction d'eau dans le mélange réactionnel, avant action de l'hydroxyde, empêche l'apparition de la coloration.

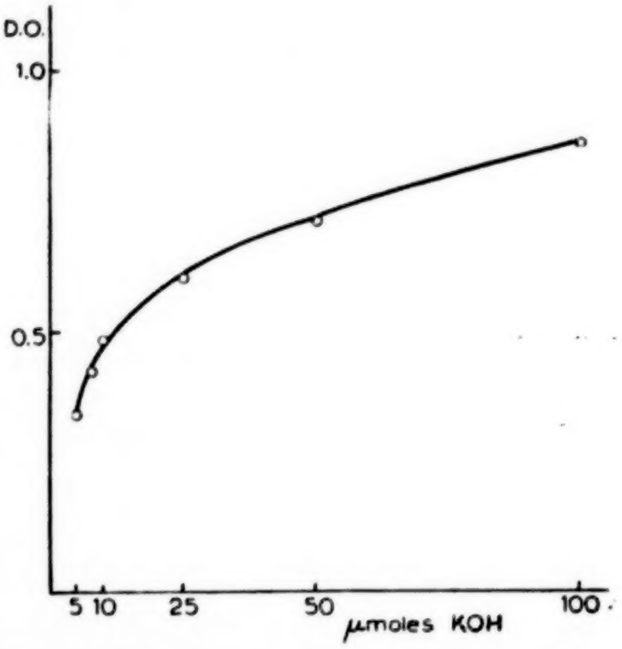


Fig. 1. Variation de l'intensité de coloration donnée par 0.2 ml de β-mercapto-éthanol $10^{-3}M$ et 0.2 ml de N-éthyl-maléimide $5.10^{-2}M$ en fonction de la quantité d'hydroxyde. Volume final: 5 ml. Densité optique à 515 mμ.

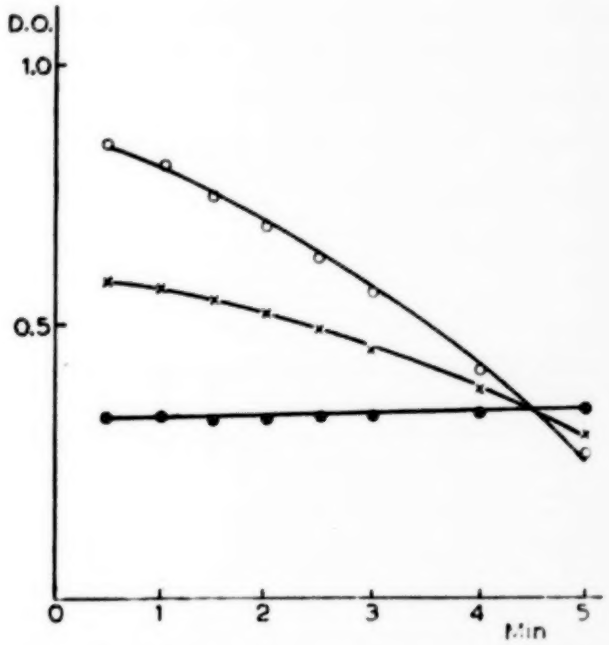


Fig. 2. Variations de l'intensité de coloration donnée, à 515 mμ, par 0.2 ml de β-mercapto-éthanol $10^{-3}M$ et 0.2 ml de N-éthyl-maléimide $5.10^{-2}M$, avec trois concentrations en KOH. Volume final: 5 ml. —●—●—●—●— 5 μM KOH, —x—x—x—x—x— 25 μM KOH, —○—○—○—○—, 100 μM KOH.

Effet de la concentration du réactif

En travaillant sur 0.2 ml de réactif à diverses concentrations, en présence de 0.05 μM de β-mercapto-éthanol et de 1 ml de KOH $N/40$, on observe que la coloration obtenue augmente en fonction de la concentration en réactif (Fig. 3) et que la stabilité s'améliore également (Fig. 4). Au-delà d'une concentration critique, le rendement en produit coloré s'abaisse, et la stabilité reste inchangée. Le rendement colorimétrique est rétabli lorsque la quantité d'hydroxyde est élevée. Ces faits tendent à prouver que la destruction de l'excès de réactif consomme l'hydroxyde rapidement, provoquant une ionisation incomplète, mais améliorant la stabilité du produit coloré. Enfin, dans le même ordre d'idées, on peut également rétablir le rendement coloré, lorsque l'hydroxyde est limitant, en diluant avec de l'eau et non de l'alcool.

Action de l'alcool sur la réaction

Le produit de la réaction de l'alcool sur la maléimide, en présence d'hydroxyde[9], possède un spectre identique à celui donné par les thiols. La quantité absolue d'alcool utilisée doit donc être maintenue constante pour que le blanc ait toujours la même valeur. L'existence de cette réaction compétitive limite l'application du dosage à environ 0.01 μM de thiol, dans les conditions décrites plus loin. Au-dessus de cette valeur, l'action de l'alcool peut être négligée (Fig. 5).

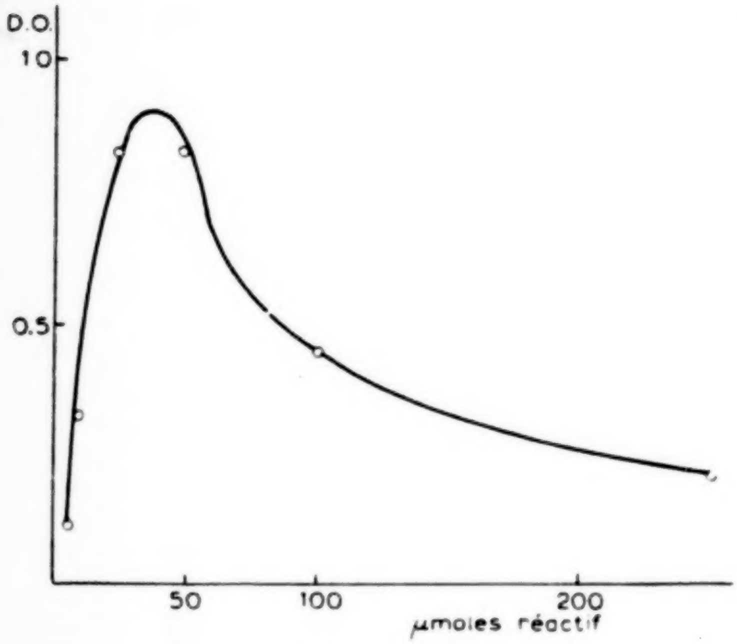


Fig. 3. Variation de l'intensité de coloration obtenue, à 515 mμ, par 0.05 μM de β-mercaptoéthanol avec diverses quantités de N-éthylmaléimide et 1 ml de KOH $N/40$. Volume final: 5 ml.

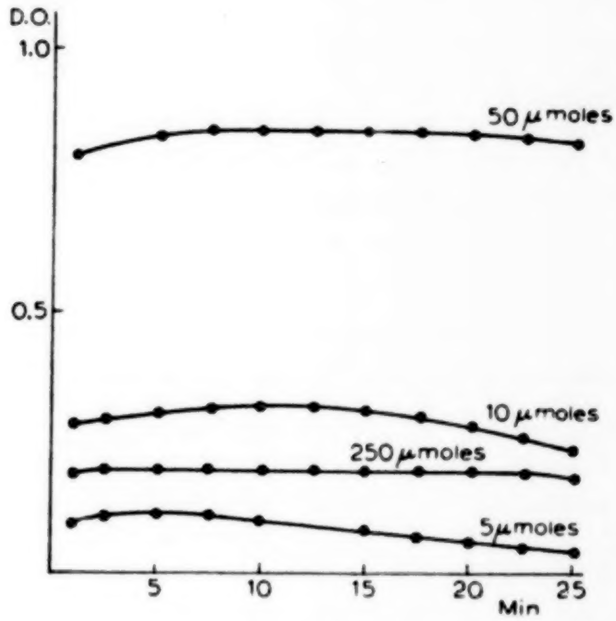


Fig. 4. Variations de la stabilité de coloration donnée, à 515 mμ, par 0.05 μM de β-mercapto-éthanol, avec quatre concentrations de N-éthyl-maléimide et 1 ml de KOH $N/40$. Volume final: 5 ml.

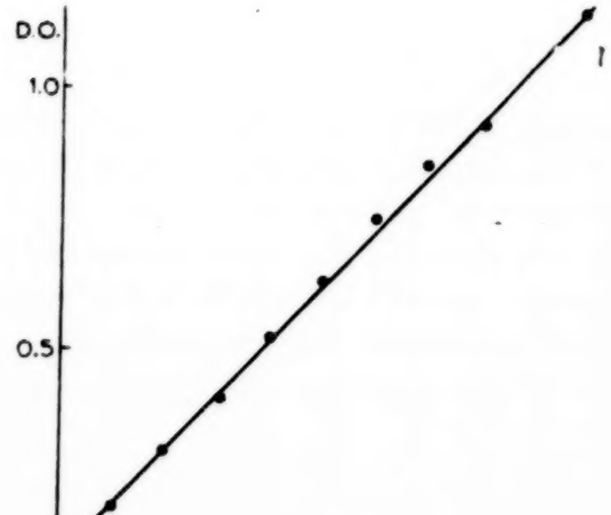


Fig. 5. Dosage d'un thiol par la N-éthyl-maléimide. 0.2 ml réactif $M/2$ dans l'isopropanol, 1.0 ml solution à doser dans l'isopropanol, 1.0 ml KOH $N/40$ dans l'isopropanol, dilué à 5 ml avec isopropanol, densité optique à 515 μM.

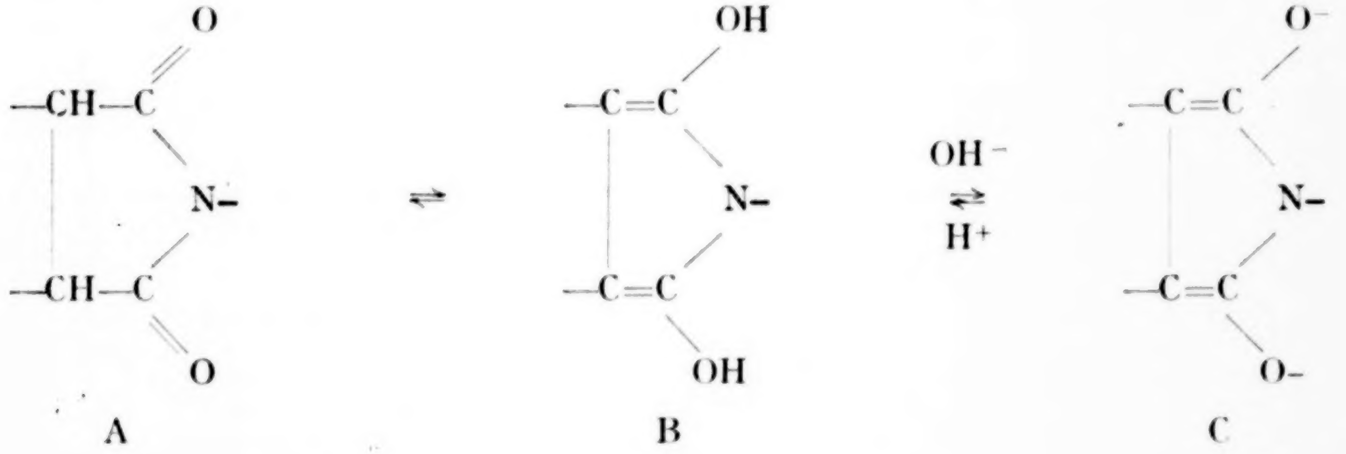
Technique de dosage

Dans un petit tube à essai, on introduit 0.2 ml de N-éthyl-maléimide $M/2$ dans l'isopropanol. On ajoute 1 ml de la solution à doser (dans l'isopropanol) et on attend 4 ou 5 min. On ajoute ensuite 1 ml d'hydroxyde de potassium $N/40$ dans l'isopropanol, on agite et on ajoute 2.5 ml d'isopropanol pour diluer la teinte. On mesure la densité optique à 515 mμ, 10 min après addition de l'hydroxyde. La loi de Beer est vérifiée entre 0.01 et 0.1 μM de thiol (Fig. 5) et la coloration est stable pendant 15 min après addition de l'hydroxyde.

DISCUSSION

On sait qu'en milieu aqueux, la réaction de la maléimide sur les thiols est rapide et irréversible[3]. Il semble qu'en milieu alcoolique, la réaction soit beaucoup plus lente, puisqu'il faut un très grand excès de maléimide pour que la réaction soit complète en quelques minutes.

Ainsi que BENESCH *et al.* le mentionnent[8], le colorant formé est un indicateur de pH. Nous avons montré que la coloration s'intensifie en milieu aqueux lorsque l'hydroxyde était un facteur limitant en milieu alcoolique: il est donc probable que la substance colorée soit un cation. Un cation dérivant d'un complexe maléimidique pourrait se concevoir simplement comme la forme (bis-)énolique de la (di-)cétone correspondante:



La forme B, beaucoup moins stable que la forme A, pourrait être le précurseur de C en présence d'un agent alcalinisant. Les réactions A ⇌ B (tautomérisation) et B ⇌ C (ionisation) seraient probablement très rapides.

La coloration n'est pas très stable. Elle se stabilise lorsque l'on diminue la concentration de l'agent alcalinisant, mais au détriment de l'intensité. L'agent alcalinisant (en grand excès par rapport au composé à former) est utilisé compétitivement par la maléimide en excès. On pourrait schématiser comme suit la série de réactions qui font partie de ce dosage:

$$\begin{tikzcd}
\text{thiol} + \text{maléimide} \arrow[r, "\text{(lent)}", "\text{(a)}"'] \arrow[dd, "\text{OH}^-"', "\text{(e) (rapide)}"] & \text{complexe A} \arrow[r, shift left, "\text{(tautomérie)}"] & \text{complexe B} \arrow[l, shift left, "\text{(b)}"] \arrow[d, shift right, "\text{OH}^-"'] & \\
 & & \text{complexe C} \arrow[u, shift right, "\text{(c) H}^+ \text{ (ionisation)}"'] \arrow[d, "\text{(d) OH}^- \text{ (lent)}"] & \text{(coloré)} \\
\text{maléimide détruite} & & \text{composé détruit} &
\end{tikzcd}$$

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Lors de la mise au point de ce dosage, il est donc très important de régler les quantités d'hydroxyde en fonction de l'excès de maléimide présente et de la quantité de complexe à ioniser après énolisation, de manière à ce que l'excès de l'hydroxyde soit suffisamment faible pour que la réaction (d) soit minimisée.

PARTIE EXPÉRIMENTALE

Produits

Toutes les substances utilisées au cours de ce travail étaient de la marque MERCK ou de la marque U.C.B. et de la qualité ,,pour analyse'', sauf:
N-éthyl-maléimide: Schwartz Lab. Inc.
Ether diéthylique: rectifié sur sodium.
Formamide: Merck, sans spécification.
N,N-diméthylformamide: produit de synthèse fraîchement distillé et rectifié.
Ethylène-glycol: Merck, sans spécification.
Méthoxyéthanol: Hopkin and Williams, fraîchement distillé.
Dioxane: fraîchement rectifié.
Ethanolamine: Eastman Kodak (dans les expériences avec cette substance, l'intensité de coloration propre du solvant a été déduite des densités optiques lues; le produit était jaune clair).
Cyclohexane: Merck, pour chromatographie.
Ether di-isopropylique: distillé sur sodium.
Eau: bidistillée dans un appareil en Pyrex.

Appareillage

Les colorations ont été déterminées à l'aide du spectrophotomètre Beckman, modèle B, dans des cuvettes de 10 mm.

RÉSUMÉ

Une technique a été mise au point pour le microdosage colorimétrique des thiols. Elle est basée sur l'action de la N-éthyl-maléimide en milieu alcoolique anhydre (isopropanol) suivie d'alcalinisation à la potasse. Les conditions assez délicates du mode opératoire sont décrites. Un mécanisme de réaction a été ébauché. Le principal intérêt de cette technique réside dans sa haute sensibilité (jusqu'à 10^{-8} mole).

SUMMARY

A new method is described for the microdetermination of thiols. It is based upon the reaction of N-ethyl-maleimid on -SH groups in absolute isopropanol. On the addition of alcoholic potassium hydroxide, a bright red color develops, which absorbs near 5150 Å. The reaction is very sensitive towards the experimental conditions; these are fully described. A scheme for the mechanism of the reaction has been proposed. The most important fact about this method lies in its very high sensitivity (up to 10^{-8} mole of thiol per trial).

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Reçu le 21 mars 1958

ESTIMATION OF TRACES OF NICKEL IN SODIUM METAL

by

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INTRODUCTION

The dimethylglyoxime method, used extensively for the absorptiometric determination of traces of nickel[1-4], suffers from many interferences[3]. In addition the colour is unstable and must be measured soon after development. Most interferences may be removed by extraction of the nickel dimethylglyoxime complex with chloroform. It was found in this laboratory that the extraction procedure must be controlled very carefully to obtain reproducible results.

BRUMMET AND HOLLWEG[5] used 0.5% potassium cyanide solution to selectively dissolve nickel from oxidized films on nickel metal. The nickel complex was then determined spectrophotometrically at 268 mμ. This method was studied in order to determine whether it could be applied to the estimation of μg quantities of nickel in metallic sodium.

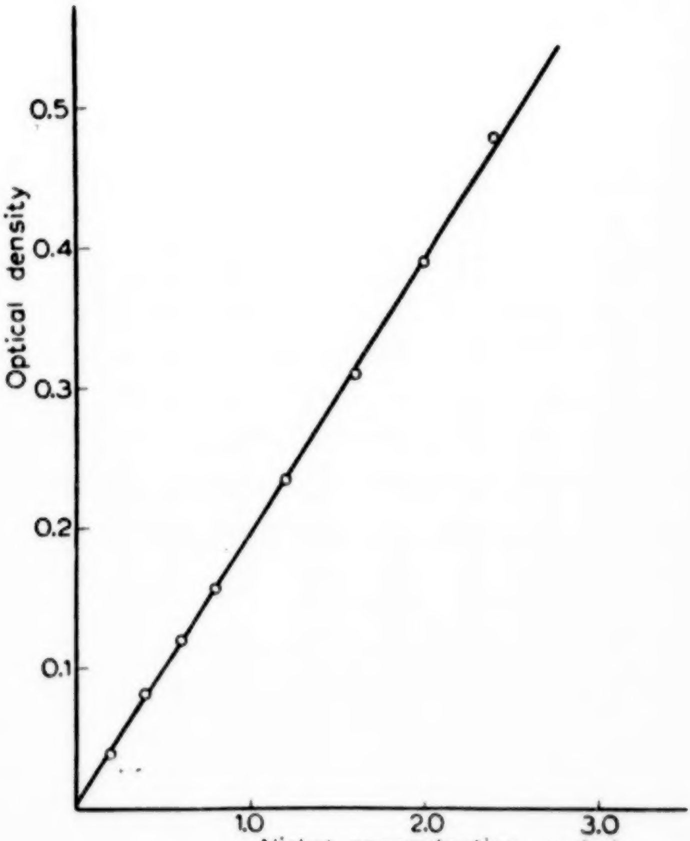

Fig. 1. Determination of nickel by the cyanide method.

EXPERIMENTAL

Optical densities were measured in 1-cm matched quartz cells with a Hilger "Uvispek" spectrophotometer.

Reagents

Standard nickel solution, prepared from "AnalaR" nickel sulphate heptahydrate. This salt was analysed by precipitation of the nickel as dimethylglyoxime and found to be 99.3% pure.

5% *w/v Potassium cyanide* prepared from "AnalaR" potassium cyanide. This chemical should have as low a ferrocyanide content as possible, and the solution should be freshly prepared every few days.

All other reagents used were of A.R. quality.

Preparation of standard curve

The required aliquot of the standard nickel solution was measured from a micro burette into a 25-ml volumetric flask. 5% potassium cyanide (2.5 ml) was added and the mixture diluted to volume. The absorbance was measured at 268 mμ with 0.8 mm slit width.

Fig. 1 shows that Beer's Law is obeyed to nickel concentrations of at least 2.4 μg/ml. The solutions were found to be stable for at least two days, and unaffected by variations in the cyanide content from 0.1 to 0.5%. The concentration of 0.5% was adopted, however, since the interferences of copper and chromium appeared less pronounced in the stronger solution.

Study of interferences

The procedure given above was used in the presence of some common cations (Table I). In addition, the following metals gave precipitates in 0.5% KCN: Fe(III) Fe(II), Be, Pb, Sn, Zn, Mn, Zr, U.

Of the common anions, only ferrocyanide was found to interfere.

TABLE I

INTERFERENCE OF SOME CATIONS

Addition per ml	*Nickel equivalent (μg/ml)*
50 mg Na	0.00
2 mg Ca	0.00
50 mg NH$_4$	0.00
2 mg Ag	0.03
5 mg Al	0.00
5 mg Ce(IV)	0.02
5 mg Cd	0.00
100 μg Fe(III) tartrate	0.56
10 μg Cu(II)	0.40
10 μg Cu(I)	0.19
3 μg Co	1.73
5 μg Mo(VI)	0.73
1 μg Cr(VI)	0.22
5 μg Cr(III)	0.10

The interference of iron, chromium and copper was studied in detail, since these elements, particularly iron and chromium, are likely to be encountered in the analysis of sodium from stainless steel loops.

Removal of iron

Rapid precipitation of iron with ammonium hydroxide was found to cause severe losses of nickel, probably by adsorption on the voluminous precipitate. If the precipitation is carefully controlled[6], by very slow addition of ammonia, the losses are greatly reduced. A double precipitation in this manner ensures complete recovery of the nickel. Double precipitation may be avoided, however, by separation of the ferric hydroxide in homogeneous solution[7] with urea (Table II).

TABLE II

PRECIPITATION OF IRON

Method of precipitation of iron (0.5 mg)	*Ni taken (µg)*	*Ni found (µg)*
Rapid precipitation with ammonia	1.00	0.10
Slow single precipitation with ammonia	1.00	0.96
Slow double precipitation with ammonia	1.00	1.01
Single precipitation with urea	1.00	1.00

Removal of chromium

As shown in Table I, chromate ion absorbs strongly at 268 mµ[8]. If, however, chromate is reduced to chromic ion the interference is decreased considerably. Any chromate originally present will be reduced by alcohol in the preparation of the sample. Chromium(III) will be removed with iron in the urea precipitation.

Removal of copper

The cupricyanide complex absorbs weakly at 268 mµ (Table I). This absorbance may be further decreased by 50% by reduction with hydroxylamine hydrochloride.

Procedure for the determination of nickel in sodium in the presence of iron, chromium and copper

Solution of the sample. Dissolve a weighed amount of the sodium sample in absolute ethyl alcohol. Small amounts of water may be cautiously added to accelerate solution. Add concentrated hydrochloric acid to the sodium alcoholate until neutral, then 5 ml in excess. Evaporate on a water bath to dryness. Bake in an air oven for 2 h at 120°. Dissolve the residue in the minimum amount of hot 0.1*N* hydrochloric acid, transfer to a volumetric flask, and make up to volume when cool.

Determination. Dilute an aliquot containing 5–75 µg of nickel to approximately 10 ml with distilled water. Add one drop of concentrated nitric acid and boil for a few minutes to oxidize iron. Add 0.5 g of ammonium chloride and 0.5 g of urea. Boil the solution gently until the pH has risen to 6–7, as tested by universal indicator paper. Simmer gently for a further 15 min to complete precipitation of chromium. Filter through a 4.5-cm No. 1 Whatman paper, and wash four times with 1-ml portions of hot 1% ammonium chloride. Add 5 drops of 10% hydroxylamine hydrochloride to the filtrate and boil gently for a few minutes. Add 2.5 ml of 5% potassium cyanide to the cold solution and dilute to 25 ml with distilled water.

Compare at 268 mµ against a standard nickel solution treated in the same manner, and using 0.5% potassium cyanide solution containing hydroxylamine hydrochloride as a reference solution.

SUMMARY

A simple and sensitive method is described for the determination of traces of nickel in sodium metal. The nickel is complexed with potassium cyanide and the absorption measured spectrophotometrically at 268 mµ.

Interference of iron and chromium is removed by precipitation of the hydroxides from homogeneous solution. This method should be applicable to a wide range of materials.

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Received March 31st, 1958

EDTA TITRATIONS WITHOUT METAL INDICATORS

by

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Ethylenediaminetetraacetic acid (EDTA) is probably the most outstanding analytical reagent of recent times. There is not a single area of analytical chemistry where this reagent has not been used with advantage. In view of the recently published book by WELCHER[1] and the series of review articles by BARNARD, BROAD AND FLASCHKA[2], no attempt will be made to review the various applications of EDTA. BARNARD, BROAD AND FLASCHKA[2] have quite exhaustively discussed the various methods of end-point detection.

The principal disadvantage in EDTA titrimetry is to find a suitable metal indicator. In general, these so called metal indicators are organic compounds which form colored complexes with metals. The theory and requirements of a suitable metal indicator have been discussed by BARNARD, BROAD AND FLASCHKA[2]. The versatility of EDTA titrimetry is greatly limited by the necessity of the large number of indicators required by the various metals.

A general procedure is described for determining the metals whose EDTA complexes have log K values of 15 or higher. The blue color formed by cobalt thiocyanate complex in acetone–water mixture serves to detect the end-point. SEN SARMA[3] has described a method for determination of cobalt using the same principle. He has also described the end-point detection using an immiscible solvent. The possibility of titrating calcium, lead and thorium using the discharge of the blue color of cobalt thiocyanate complex in an immiscible solvent has been indicated[3]. SEN[4,5] has estimated potassium, rubidium, cesium, thallium and ammonium by determining the cobalt with EDTA in a precipitate of $M_2NaCo(NO_2)_6$ or $M'_2AgCo(NO_2)_6$ (M = potassium, M' = potassium, rubidium, cesium, thallium or ammonium). It has been found during the course of present investigations that the end-point in cobalt determination is much sharper when EDTA solution containing thiocyanate and acetone, and adjusted to proper pH, is titrated with cobalt. Using this procedure, the solution becomes more and more pink until the equivalence point, and then turns distinctly blue with one drop (0.025 mg) excess of cobalt solution in a total volume of 100 ml. This amount of cobalt, used as an indicator for titration directly with EDTA does not give a sharp end-point. According to the procedure briefly described above, the requirement of pH adjustment is not rigorous as suggested by TAKAMOTO[6]. Identical titers are obtained with pH anywhere between 6 and 12 (*cf.* Table I).

The general procedure for titrating metals whose EDTA complexes have log *K* values of 15 or higher is as follows: The metal solution is added to a measured excess of EDTA solution and its pH is then adjusted to 7 with ammonium acetate and 1 ml of a saturated solution of ammonium thiocyanate is then added, followed by acetone. The ratio of acetone to water should be approximately one to one at the end of the titration. The solution is then titrated to the first appearance of the permanent bluish tint throughout the solution.

TABLE I

DETERMINATION OF COBALT

Vol. of EDTA = 10 ml

Cobalt titer ml	*pH*	*Masking agent*	*Cobalt taken mg*	*Cobalt found mg*
10.7	6		5.92	5.92
10.7	7		5.92	5.92
10.7	8		5.92	5.92
10.7	9		5.92	5.92
10.7	10		5.92	5.92
10.7	12		5.92	5.92
10.7	7	1 g Rochelle salt	5.92	5.92
10.7	7	1 g Oxalic acid	5.92	5.92
10.7	7	1 g Ammonium citrate	5.92	5.92

EXPERIMENTAL

All chemicals used were of analytical reagent grade.

Standard solution

EDTA solution (0.01M). Disodium ethylenediaminetetraacetate was directly weighed to prepare the standard solution.

Approximately 0.01M solutions of different metals were prepared from cobalt nitrate, nickel sulfate, lead nitrate, vanadyl sulfates, sodium metavanadate and thorium nitrate. The strength of each solution was determined according to standard procedure.

Determination of cobalt at various pH

10 ml of EDTA solution was taken in a 250-ml Erlenmeyer flask and its pH was adjusted using any of the following: acetic acid, ammonium acetate, sodium carbonate, or 0.1N sodium hydroxide solution. pH paper was used to indicate the pH. For pH 7, 0.5–1 g of solid ammonium acetate was used. 1ml of a saturated solution of ammonium thiocyanate was then added, followed by 25 ml of acetone. The solution was then titrated with 0.01M cobalt nitrate solution until the first permanent bluish tint appeared throughout the solution. The presence of common masking agents, such as tartrate, citrate, and oxalate do not interfere with the determination of cobalt; cyanide, however, seriously interferes.

Determination of thorium, lead, nickel and vanadium (VO^{+2})

To the solution (5–10 ml) of the metal as sulfate, nitrate or chloride is added a measured excess of standard (0.01M) EDTA solution (15 ml). If the solution is too strongly acidic, the excess of acid is neutralized with sodium carbonate and the pH is finally adjusted by adding ammonium acetate (1 g). To the solution is then added a saturated solution of ammonium thiocyanate (1 ml) and acetone. The volume of the acetone added should be such that the water–acetone ratio at the end-point is approximately one to one. However, the water–acetone ratio may be adjusted during the titration. The excess of EDTA is then titrated with $0.01\,M$ cobalt nitrate solution to the first permanent bluish tint throughout the solution. The end-point is reversible. So if the end-point is missed, some more EDTA is added and back titrated with cobalt. For the sharpness of the end-point, the excess of EDTA should be enough to react with 5 ml or more of $0.01\,M$ cobalt solution. The results are given in Table II.

Determination of vanadate

To 10 ml of vanadate solution containing 3–5 mg vanadium is added an excess of standard EDTA solution. The mixture is then slightly acidified with a few drops of glacial acetic acid. Ascorbic acid (0.1–0.5 g) is then added to the solution and heated nearly to boiling and kept at that temperature for about a minute to complete the reduction of vanadate to vanadyl. The solution is then cooled and ammonium acetate (1 g) is added, followed by 1 ml of a saturated solution of ammonium thiocyanate and proper amount of acetone. The excess of EDTA is then, as usual, titrated with cobalt. Reduction of vanadate can be done also with hydroxylamine hydrochloride. The results are shown in Table III.

TABLE II

Cation estimated	*Cobalt titer* *ml*	*Cation taken* *mg*	*Cation found* *mg*
Th^{+4}	5.50	22.84	22.86
	5.50	22.84	22.86
	5.50	22.84	22.86
	5.50	22.84	22.86
	5.50	22.84	22.86
Pb^{+2}	5.50	20.30	20.40
	5.50	20.30	20.40
	5.50	20.30	20.40
	5.50	20.30	20.40
Ni^{+2}	6.85	5.05	5.07
	6.90	5.05	5.40
	6.85	5.05	5.07
	6.90	5.05	5.04
	6.90	5.05	5.04
VO^{+2}	9.80	3.039	3.04
	9.80	3.039	3.04
	9.80	3.039	3.04
	9.80	3.039	3.04

TABLE III

Reducing agent	*Cobalt titer* *ml*	*Vanadium taken* *mg*	*Vanadium found* *mg*
Ascorbic acid	8.30	3.76	
	8.20	3.76	3.76
	8.20	3.76	3.76
	8.20	3.76	3.76
Hydroxylamine hydrochloride	8.20	3.76	3.76
	8.20	3.76	3.76
	8.20	3.76	3.76

Determination of vanadate and vanadyl

In a mixture of vanadyl (VO^{+2}) and vanadate (VO_3^-), vanadyl is determined by the method described earlier and vanadate does not interfere. Vanadate is then reduced by ascorbic acid or hydroxylamine hydrochloride and the total vanadium is then determined as vanadyl as described. Table IV shows some typical data.

TABLE IV

VO^{+2} *taken* *mg*	VO^{+2} *found* *mg*	VO_3^- *taken* *mg*	VO_3^- *found* *mg*
1.52	1.52	1.88	1.90
1.52	1.52	1.88	1.90
1.52	1.52	1.88	1.90

DISCUSSION

The procedure described here is very simple, rapid and highly accurate for the estimation of cations reported in this paper, as well as for all other cations having log *K* values equal to or greater than 15. Mercury and copper are among the few exceptions. Mercury forms a very stable complex with thiocyanate and the color of the copper–EDTA complex interfere with the end-point detection. The conditions of determination are not all rigorous.

During the determination of vanadate, it has been found that vanadate can be easily and completely reduced with ascorbic acid or hydroxylamine hydrochloride in the presence of EDTA. Use of sodium sulfite is unnecessary[7].

Among the anions, cyanide can be determined by a slight modification of the procedure described for the cations. The results of the determination of other cations, mixtures of cations and cyanide will be described in a subsequent communication.

ACKNOWLEDGEMENT

The author expresses his deep sense of gratefulness to Prof. PH. W. WEST, Boyd Professor of Chemistry, Louisiana State University, for providing all the facilities to carry out the present investigations. Thanks are also due to Dr. B. R. SANT of Banaras Hindu University for his help and useful suggestions.

SUMMARY

A general method of estimating metals whose EDTA complexes have log *K* values of 15 or higher has been proposed. The metals are complexed with excess EDTA, and the excess is titrated with standard cobalt solution in acetone–water system containing ammonium thiocyanate and adjusted to pH 7.

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Received April 14th, 1958

DETERMINATION OF THALLIUM BY A DITHIZONE MIXED-COLOR METHOD*

by

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INTRODUCTION

The present investigation was undertaken to find a direct and sensitive colorimetric method for the determination of thallium in relatively pure solutions. A procedure of this type was required for a contemplated study of the absorption of metal ions from solution by various minerals. Neither ANDERSON's[1] thorough review of the analytical chemistry of thallium nor a search of the more recent literature led to a procedure that seemed to satisfy our requirements.

The most commonly used colorimetric method for the determination of small quantities of thallium has been based largely on the reports of HADDOCK[2] and SILL AND PETERSON[3]. Thallium(III) is reacted with iodine and the final color measurement made on the starch–iodine system. This procedure has the disadvantages inherent in an indirect measurement of thallium concentration and the instability of the starch–iodine system.

FISCHER AND WEYL[4] presented the absorption spectrum of a carbon tetrachloride solution of thallium(I) dithizonate which had been extracted from a solution containing potassium cyanide. Subsequently, dithizone has been used as a means of separating thallium from other elements, but it has not been used as a colorimetric or spectrophotometric reagent for thallium. However, it has been used as a "limit test" by BAMBACH[5], where total lead and thallium are determined together in pharmaceutical chemicals by colorimetric comparison of dithizone solutions.

SANDELL[6] suggested that dithizone could be used as a reagent for the determination of thallium. An investigation of this system was undertaken because dithizone offers the advantages of a single reagent being used for the separation, concentration, and the direct measurement of thallium. A procedure based on it would also be of comparable sensitivity to that found in other metal–dithizone systems.

Extraction with dithizone from an alkaline solution containing cyanide and citrate separates thallium from usual concentrations of elements other than lead, bismuth, and tin(II). These interferences would be insignificant in the solution in which we were interested and it was thought that by properly selecting separations this method could later be applied to materials of geologic interest. MAYNES AND MCBRYDE[7] have shown that extraction with diethylammonium diethyldithiocarbamate can be used to separate thallium from lead and bismuth.

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* Publication authorized by the Director, U.S. Geological Survey.

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During the course of this work a number of papers have been published on the use of other colorimetric agents for the determination of thallium. GUR'EV[8] has reported a procedure using methyl violet and GUR'EV AND SHKROBOT[9] one using crystal violet. VOSKRESENSKAYA[10] has reported on the use of both methyl violet and Brilliant Green. GLADYSHEV AND TOLSTIKOV[11] have used *p*-aminophenol, and POHL[12] has made use of the absorption of ether solutions of thallium carbamate. ONISHI[13] has developed a procedure using Rhodamine B.

APPARATUS AND REAGENTS

Apparatus

Spectrophotometer. All absorbance measurements were made with a Beckman DU spectrophotometer using 1-cm corex cells. The absorption spectra were recorded with an automatic attachment.

pH meter. A line-operated pH meter with a special high-pH glass electrode and a sleeve-type calomel electrode was used.

Shaking machine. A wrist-action laboratory shaking machine was used.

Reagents

Water. Redistill water from an all glass still. *Thallium nitrate solution.* (1.00 mg Tl/ml). Dissolve 1.303 g of thallous nitrate in redistilled water and dilute to a liter. This solution is diluted to a convenient concentration just prior to use. *Sodium citrate, 25% (w/w).* Dissolve 250 g of reagent-grade sodium citrate in 750 g of redistilled water. *Sodium sulfite, 5% (w/w).* Dissolve 25 g of reagent-grade (A.C.S.) sodium sulfite in 475 g of redistilled water and store in a polyethylene bottle. *Potassium cyanide, 5% (w/w).* A purified potassium cyanide solution is prepared according to the procedure of SANDELL[14]. This solution should be stored in a polyethylene bottle. *Chloroform.* Reagent-grade (A.C.S.) chloroform is redistilled with an all glass still. *Dithizone.* Purify dithizone by the procedure of SANDELL[15]. Store dithizone solutions in red low actinic glass bottles in a refrigerator. *Dithizone solution No. 1.* (1.2 mg dithizone/15 ml). Dissolve 80 mg of purified dithizone in 1 l of redistilled chloroform. *Dithizone solution No. 2.* (0.4 mg of dithizone/15 ml). Dissolve 27 mg of purified dithizone in 1 l of redistilled chloroform. *Nitric acid, 0.08N.* Dilute 5.0 ml of reagent-grade nitric acid which has been redistilled with an all glass still to 1 l with redistilled water. *Sodium hydroxide, 0.08N.* Dissolve 3.2 g of reagent grade (A.C.S.) sodium hydroxide in 1 l of redistilled water. Store in a tightly closed polyethylene bottle.

RECOMMENDED PROCEDURE

The procedure found most successful is the double extraction procedure given in detail here.

Transfer an aliquot of a neutral thallium solution to a 60-ml separatory funnel which has a Teflon stopcock. Add 5.0 ml of 25% sodium citrate, 1.0 ml of 5% sodium sulfite, 2.0 ml of 5% potassium cyanide, and enough water to make a total volume of 20 ml (Tl solution plus H_2O equals 12 ml). Add 15.0 ml of dithizone solution No. 1 (1.2 mg of dithizone) and shake for 10 min on a shaking machine.

Allow the two layers to separate for several minutes and then drain the chloroform layer into a clean 60-ml separatory funnel. Rinse the stem of the first separatory funnel by passing 2 ml of chloroform through the funnel. Wash the water layer twice more by shaking by hand for about 10 sec with 3-ml portions of chloroform. Collect all of the washings in the second separatory funnel taking care to empty the stem of the first separatory funnel each time chloroform solution is drained off.

Strip the thallium from the chloroform solution in the second separatory funnel by shaking with 0.08*N* nitric acid. To do this add 15.0 ml of 0.08*N* nitric acid to the separatory funnel containing the chloroform solution and shake on a shaking machine for 5 min. Allow the two layers to separate for several minutes and then drain off the chloroform layer and discard it. Wash the water layer as before by first rinsing with 2 ml chloroform and then wash twice more with 3-ml portions of chloroform being careful not to lose any of the water layer.

Neutralize the nitric acid solution in the separatory funnel by titrating with 0.08*N* sodium hydroxide. For this step add 0.05 ml of approximately 0.1% methyl red to the solution in the separatory funnel (the methyl red must be added carefully from a pipette as it contributes to the blank). Add the sodium hydroxide from a burette until the first definite yellow end-point is reached. Add 2.0 ml of 5% potassium cyanide, followed by 15.0 ml of the dilute dithizone solution No. 2 (0.4 mg dithizone) which has been allowed to warm to near room temperature. Extract by shaking

for 10 min on a shaking machine. Insert a filter plug made by rolling half a circle of 5.5 cm close textured filter paper into the stem of the funnel. Draw off and discard the first 1 - 2 ml of chloroform solution and collect most of remainder in a small glass-stoppered flask. Measure the absorbance against chloroform as a reference solution at 505 mμ using 1-cm cells.

DISCUSSION OF EXPERIMENTAL CONDITIONS

In preliminary experiments the absorption spectra of the thallium-dithizone system were obtained at a number of thallium concentrations. These data were the basis for development of a procedure for determining thallium. A citrate-sulfite-cyanide medium was selected for the extraction of thallium dithizonate from aqueous solution and the effects of various factors on this system were studied.

A procedure involving two extractions with dithizone is recommended over a single extraction from the citrate-sulfite-cyanide medium for two reasons. The double extraction procedure is somewhat more sensitive and more reproducible results are obtained. The increase in reproducibility undoubtedly results from the more readily controlled conditions in the solution from which the final extraction is made.

Preliminary experiments

Absorption spectra. The absorption spectra of the thallium-dithizone mixed-color system obtained in preliminary experiments are given in Fig. 1. The solutions from which these curves were obtained were made by extracting an aqueous solution of thallium with 15.0-ml portions of a chloroform solution of dithizone which contained 0.3 mg of dithizone per 15 ml. The aqueous solutions were made to a total volume of 20 ml. They contained various amounts of thallium, 3 ml of 6% hydroxylamine hydrochloride, and their pH was adjusted to 10.2 by the addition of 2*N* sodium hydroxide. After the extraction was completed, the chloroform solutions were filtered through a filter paper plug in the stem of the separatory funnel into a glass-stoppered flask. These solutions were used directly to obtain absorption spectra with a recording spectrophotometer. Chloroform was used as a reference and measurement was made in 1-cm cells.

In Fig. 1, curve 1 represents the absorption spectrum of a chloroform solution of

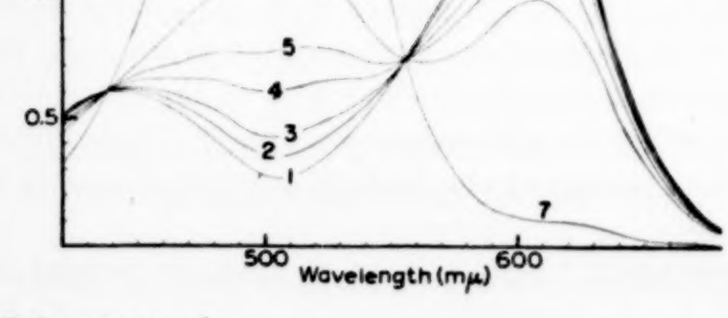

Fig. 1. Absorption spectra of Tl-dithizone mixed-color system. (Chloroform reference, 1-cm cells).

Curve	*Tl, μg*
1	0
2	10
3	20
4	40
5	60
6	100
7	1000

dithizone, and it has a minimum at 502 mμ and a maximum at 606 mμ. Curve 7 represents the absorption spectrum of pure complex, and it has a maximum at 512 mμ and a minimum at 400 mμ which is not shown in the figure. These curves are essentially the same as those given by FISCHER AND WEYL[4]. Curves 2 through 6 are for various levels of thallium.

In Fig. 1 there are isoabsorptive points shown at 438 and 555 mμ. A third isoabsorptive point was observed at 390 mμ. This type of absorption spectrum is a criterion for the existence of an equilibrium between two absorbing species (WEST[16]). This would indicate that equilibrium exists between a single thallium-dithizone complex and dithizone under the conditions of this experiment.

Fig. 1 also shows that the absorption peaks for the thallium-dithizone complex and for dithizone are well separated. The region of each of these peaks is particularly suitable for relating absorbance measurements to thallium concentration. Measurement of the increase in absorbance due to complex formation can be made from 505–515 mμ. Measurement of the decrease in absorbance due to disappearance of dithizone can be made from 600–610 mμ. A plot of data taken from Fig. 1 at selected wavelengths within these regions is given in Fig. 2. The curve at 505 mμ is considerably more sensitive and conforms to Beer's law. The curve at 606 mμ shows slight deviation from Beer's law. For these reasons all subsequent work was done at 505 mμ.

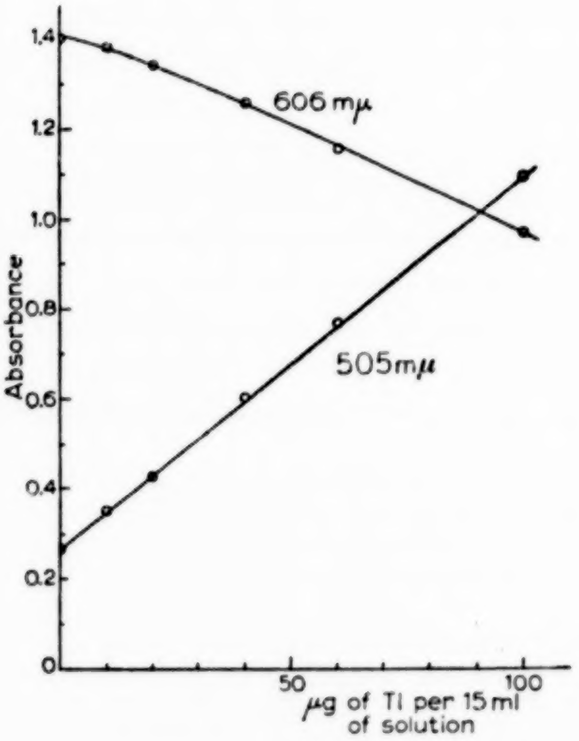

Fig. 2. Relationship of absorbance at 505 and 606 mμ to thallium concentration. (Chloroform reference, 1-cm cells).

Use of citrate and sulfite. The first extraction of thallium dithizonate is made from solutions approximately 0.2*M* in sodium citrate. The function of the citrate is to complex metals that would precipitate as hydroxides or phosphates at the high pH used (WELCHER[17]). As the presence of citrate usually has no effect on the extraction of dithizonates, no specific test of its effect on the system was made. Ammonium citrate cannot be used to replace sodium citrate at the high pH used as ammonia is evolved and variations in pH result.

Sodium sulfite is used as a reducing agent to insure that thallium is present as thallium(I) and to reduce foreign ions that might otherwise oxidize dithizone. Hydroxylamine hydrochloride has been frequently used for this purpose but was found to be unsatisfactory in this instance. It gives poorly reproducible blanks and occasional erratic absorbance readings for the thallium-dithizonate solutions.

Study of experimental variables

Studies, using single extraction with the dilute dithizone solution, were made of the factors considered in selecting the conditions recommended in the procedure. The single extraction studies gave sufficiently accurate data at a considerable saving of time.

Effect of pH and potassium cyanide concentration. WICHMAN[18] presented curves that relate the percent metal extracted by a chloroform solution of dithizone to the pH of the solution from which the metal was extracted. According to the curve given for thallium(I), thallium can be extracted somewhat at a pH slightly above 8 and completely at pH values of 10.5 or greater. Our experimental data indicated an optimum pH range of 10.3–11.5 for the chloroform extraction of thallium(I). It also showed no extraction of thallium(I) at a pH less than 7.7, thus confirming the curve WICHMAN had given earlier.

Preliminary experimental data also indicated that close control of pH would be necessary for an accurate and precise method. Within the optimum pH range, the absorbance of both the thallium complex and the reagent blank varied slightly with change of pH, the absorbance of the blank decreasing with increasing pH.

Selection of potassium cyanide for controlling pH was based primarily on its ability to buffer within the pH range chosen for the chloroform extraction. A further consideration was the desirability of having cyanide ion present to prevent the extraction of metals other than thallium(I), lead, tin(II) and bismuth (SANDELL[19]). Subsequent work on the simultaneous effect of pH and potassium cyanide concentration, was in the pH range of 9.9–11.1, the latter pH requiring use of more cyanide than would be convenient in practice.

The study of the effect of variation in potassium cyanide concentration upon extraction was made with two series of solutions each containing the recommended amount of citrate and sulfite. One series was a reagent blank and the other contained 50 μg of thallium. Amounts of 5% potassium cyanide varying from 0.5–10 ml were added to each series, and the volumes were adjusted to a total of 20 ml with water. These solutions were extracted with 15 ml of dilute dithizone solution. Absorbance measurements were made on the chloroform–dithizone extracts, and pH measurements were made on the aqueous phase. Results are shown in Fig. 3.

The curves in Fig. 3 diverge over the pH range presented and do not show the complete relationship between pH and absorbance. This incomplete picture results from the limitation in pH attainable with potassium cyanide. Earlier work using sodium hydroxide to attain higher pH values shows that the curves reach a maximum divergence at about a pH of 11.5 and then converge rapidly. At pH 12.5, the difference in absorbance between a reagent blank and the chloroform extract of the thallium(I) dithizonate is about 50% of the difference at pH 11.5.

Although consideration of Fig. 3 indicates that the greatest sensitivity would be obtained when using 10.0 ml of the cyanide solution (pH 11.1), 2.0 ml of 5% potassium cyanide (pH 10.5) was selected for the recommended procedure. Experience showed that any increase in sensitivity obtained when using larger than 2-ml amounts of cyanide solution was more than offset by loss in reproducibility of the reagent blank.

Dithizone concentration. Single extraction experiments from the citrate–sulfite–cyanide medium were performed to study the effect of variation of dithizone concentration. The differences in absorbance between samples and reagent blanks were measured. They reached a constant value at a concentration of 0.2 mg of dithizone per 15 ml of solution when 50 µg of thallium were present, and at a concentration of 0.4 mg of dithizone per 15 ml of solution when 90 µg of thallium were present.

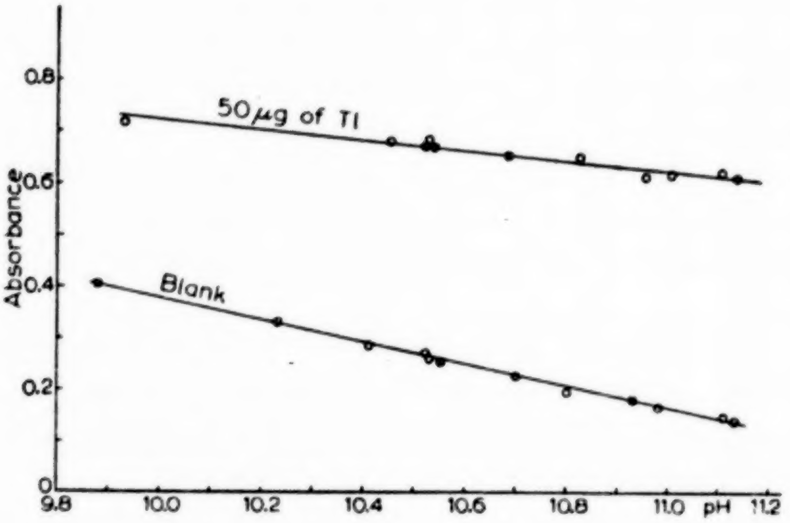

Fig. 3. Relationship between pH adjusted by variation of KCN concentration and absorbance of blanks and solutions containing 50 µg of Tl per 15 ml. (Chloroform reference, 1-cm cells, 505 mµ).

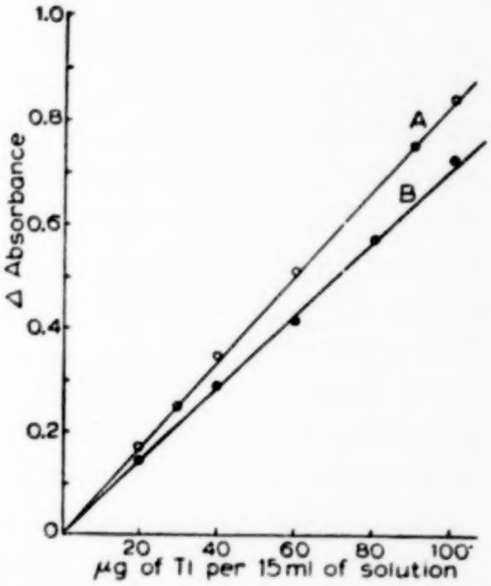

Fig. 4. Beer's law curve showing comparison of extraction procedures. A. Double extraction, B. single extraction.

Shaking time. The effect of shaking time on extraction was studied using blanks and solutions containing 20 and 60 µg of thallium. Shaking was done on a wrist-action shaker for 5-min time intervals over a period of 30 min. The resulting absorbance values were essentially constant from 5–15 min. The values seemed to rise slightly during the period from 15–30 min. A 10-min shaking period was selected, although shorter periods would undoubtedly be equally satisfactory.

Stability of complex. The stability of the complex was tested by reading absorbance values on dithizone extracts of a blank, a solution containing 50 µg of thallium, and one containing 1 mg of thallium. The latter corresponds to the solution used for pure complex in Fig. 1. Readings were made every 30 min over a 6-h period. The cell holder containing the solutions stood exposed to the artificial light of the laboratory except when readings were being taken. Absorbance values decreased rather evenly during this period for a total of about 2%. Readings made within the first two hours, however, were essentially constant and within instrumental reading error.

Acid-strip and final pH adjustment

When a chloroform solution of thallium dithizonate is shaken with 0.08*N* nitric acid, the complex is destroyed and the thallium reverts to the water layer. This acid solution is titrated with 0.08N sodium hydroxide in the separatory funnel to the first definite yellow color immediately after adding 0.05 ml of 0.1% methyl red solution from a pipette. Care must be taken in the addition of the methyl red solution prior to titration. An experiment was made using different amounts of indicator dispensed from a dropping bottle. Two drops of solution gave blanks with an average absorbance value of 0.130, while 3 drops gave 0.150 and 4 drops 0.171. If the indicator is allowed to stand in the solution too long before titration, it may extract into the small volume of chloroform that is present in the bottom of the funnel and cause difficulty in seeing the end-point.

Titration of the acid solution according to the recommended procedure results in a pH very near the neutral point. The addition of 2.0 ml of 5% potassium cyanide to these solutions leads to closely controlled pH in the vicinity of 10.6. The observed pH variation for a given set of experiments was no more than 0.1 of a pH unit. The resulting solutions are then ready for final extraction of the thallium–dithizone complex and subsequent measurement of absorbance.

The thallium is extracted from these solutions by shaking with 15.0 ml of dithizone solution added carefully from a pipette. A concentration of 0.4 mg of dithizone per 15 ml of chloroform was selected for the second extraction, as experiments given above established, this would complex at least 90 μg of thallium. The dithizone concentration selected for the first extraction is three times that used in the second. This was done to insure a large excess of the reagent in the initial separation step.

Conformity to Beer's law

Fig. 4, curve A, is a Beer's law plot of data obtained using the recommended double-extraction procedure. Values for differences in absorbance between sample and reagent blank used to plot this curve are averages of data from four experiments performed on different days. The pH values for the solution from which the extractions were made ranged from 10.6 to 10.8, although for a given day varied by no more than 0.1 of a pH unit.

The 60 μg level is the only one determined on all four days. At this thallium level the individual values for differences in absorbance differed from their average value by a maximum of 3.6 percent and an average of 2.3 percent. Four values for difference in absorbance were also obtained at the 60 μg level in a single experiment. These individual values for difference in absorbance differed from their average by a maximum of 2.7% and an average of 1.4%.

Satisfactory thallium values for some purposes could be obtained by a single extraction from the citrate–sulfite–cyanide medium which has a pH of approximately 10.6. An experiment using dithizone solution No. 2 (0.4 mg dithizone per 15 ml) where the more concentrated solution is normally used gave the Beer's law curve, curve B, in Fig. 4. This curve represents a loss in sensitivity of 13% over the double-extraction procedure. On the basis of the data at hand, the single-extraction procedure lacks the reproducibility that can be obtained with a double extraction.

CONCLUSION

Use of the thallium–dithizone mixed-color system has been shown to be a reproducible and sensitive method for thallium under properly controlled conditions. The

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only elements that would be significant interferences are lead, bismuth, and tin(II). A combination of this dithizone method of determination with published methods of separation should result in a useful analytical method for thallium in a wide variety of materials including those of geologic interest.

ACKNOWLEDGEMENT

This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission.

SUMMARY

The absorption spectra of the thallium–dithizone mixed-color system are presented and discussed. An analytical procedure based on this system is given which is applicable to pure solutions.

In the procedure thallium is extracted with a chloroform solution of dithizone from a citrate–sulfite–cyanide medium at a pH of 10.6 and then stripped from this chloroform solution with dilute nitric acid. The resulting acid solution is neutralized with sodium hydroxide and the pH again adjusted to 10.6 with potassium cyanide. A second extraction is made with dithizone and the absorbance determined at 505 mμ. Lead, bismuth, and tin(II) are serious interferences.

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Received April 14th, 1958

RAPID AND ACCURATE AUTOMATIC TITRATION OF CALCIUM AND MAGNESIUM IN DOLOMITES AND LIMESTONES

USE OF EDTA TITRANT AND AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC END-POINT TERMINATION

by

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INTRODUCTION

In order to eliminate the time-consuming classical procedures for the determination of calcium and magnesium in limestones and dolomites, there have been many attempts to develop rapid and accurate separation and titration procedures. Several different complexometric procedures using EDTA titrant have been devised for this purpose[1-7], based on the original work of BIEDERMANN AND SCHWARZENBACH[8]. The main objections to these methods have been the rather indistinct end-points and somewhat time-consuming separations of calcium and magnesium. SHAPIRO AND BRANNOCK[9] obtained the end-points more precisely by recording the indicator color changes in a photometer unit, but their over-all procedure was quite time-consuming. It is shown in the following presentation that recent complexometric indicator and automatic titrator developments can be combined to provide an automatic titration procedure requiring less than five minutes for the accurate determination of both calcium and magnesium.

MALMSTADT AND ROBERTS[10] described the applicability and advantages of the automatic derivative technique for spectrophotometric end-point detection either with or without added indicators. MALMSTADT AND VASSALLO[11] showed that a compact filter-photometer unit could be attached to the commercially available Sargent-Malmstadt automatic derivative titrator[12] to perform rapid and accurate titrations, and they performed many acid–base and redox titrations using the absorbance changes of ordinary indicators for automatic end-point termination. They also presented the general considerations for the automation of any titration procedure using spectrophotometric end-point detection, and these considerations are important for complexometric titrations with EDTA.

The new commercially available automatic Spectro-Electro titrator (E. H. Sargent Co., Chicago 30, Ill., U.S.A.) was used in this investigation and found to be well suited for rapid and accurate determinations of calcium and magnesium in limestones and dolomites as described herein. This instrument employs the automatic derivative technique for either spectrophotometric or electrometric end-point detection.

A recently reported indicator[13], known as Calcon, provides an accurate end-point signal for the EDTA titration of calcium in the presence of magnesium. The magnesium, in an aliquot of sample, is precipitated as magnesium hydroxide by addition of sodium hydroxide to adjust the pH at 12.5–13, and the calcium is automatically titrated with

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0.01N EDTA in the presence of magnesium hydroxide. Another aliquot of sample is buffered at pH 10 and both calcium and magnesium automatically titrated with Eriochrome Black T indicator, and the magnesium calculated by difference. The automatic end-points are reproducible and accurate within 0.01 ml of titrant which provides results more accurate than 0.1% of the amount present for standard samples of dolomites and limestones.

APPARATUS

The new Sargent-Malmstadt Spectro-Electro titrator was used. The filter wheel was set at the 650 mμ position, and the standard photoconductive detector circuit supplied with the unit was used, consisting of a Hupp CDS-10 cell, series resistance (5800 ohms), and dry cell (1.5 V). The standard light source, a GE 64 bulb, was used. The polarity switch was thrown to position 2, which is the correct position when there is an increase of absorbance at the end-point.

Most titrations were performed in a 50-ml beaker with the appropriate stirrer to provide maximum stirring efficiency without drawing air into the solution. A teflon stopcock, automatic zero, 10-ml buret (Fischer-Porter Co., Hatboro, Pa.) was used to deliver the titrant, and was refilled from a reservoir by gravity flow through a side arm fitted with a teflon stopcock. The delivery of titrant was adjusted to a flow rate of about 3 ml/min with either a suitable capillary delivery tip or adjustment of the teflon stopcock and pinch-off valve.

When developing the titration methods it was helpful to record the regular spectrophotometric titration curves. This was done by connecting 100 K and 10 K resistors in series, putting this combination across the "Spectro" recorder terminals, and feeding the voltage drop across the 10 K resistor to the input of a 50-mV Varian recorder. The second derivative curves can be recorded by connecting to the recorder terminals of the derivative control unit.

REAGENTS

Standard calcium solution. Dissolve 1.0009 g of primary standard calcium carbonate (Mallinckrodt Chemical Co.) in dilute hydrochloric acid solution and dilute to 1 l with double distilled or preferably de-ionized water. 1 ml contains 0.4008 mg calcium.

EDTA solution. Dry the disodium salt of ethylenediaminetetraacetic acid (EDTA) at 80°. Dissolve 3.723 g of the dried salt in de-ionized water and dilute to 1 l. Standardize this solution against the standard calcium solution and store it in polyethylene bottles.

Magnesium solution. Dissolve approximately 2.465 g magnesium sulfate heptahydrate in 1 l distilled water. Standardize the solution with EDTA using Eriochrome Black T as indicator.

Sodium hydroxide, 1N aqueous solution.

Triethanolamine, C.P.

Ascorbic acid solid.

Buffer solution. 67.5 g of reagent-grade ammonium chloride and 570 ml of C.P. concentrated ammonium hydroxide are diluted to 1 l with distilled water.

Calcium indicator (Calcon). Dissolve 0.2 g Calcon indicator (CI 202, J. T. Baker and Co.) in 50 ml methanol.

Total calcium and magnesium indicator (EBT). Dissolve 0.2 g Eriochrome Black T (CI 203, J. T. Baker and Co.) in 50 ml methanol.

GENERAL TITRATION CONSIDERATIONS

The stability constants for the calcium–calcon and calcium–EDTA complexes are $10^{5.6}$ and $10^{10.7}$, respectively. This large difference is advantageous for the automatic derivative spectrophotometric titration of calcium, because the indicator absorbance change is rather sharp, which provides a large signal for operation of the derivative control unit. The reactions are rapid and the automatic end-point is coincident with the equivalence point for titrant flow rates up to about 3 ml/min. Faster flow rates of titrant can be used, but a small blank correction is then necessary. For example, a blank correction of 0.05 ml was obtained at flow rates of 5 ml/min, and was reproducible to 0.01 ml. A buret accurate to nearly 0.005 ml was used, and it was found most convenient to select a sample aliquot requiring about 5 ml of titrant for the average sample. Consequently, the relative accuracy was about 0.1% for the average sample, and at the desirable flow rate of about 3 ml/min, a titration was automatically completed in less than 2 min.

The regular absorbance *versus* milliliters curve for the titration of calcium with EDTA titrant and calcon indicator at pH 13 is shown in Fig. 1A, together with its recorded, electronically computed second derivative curve, Fig. 1B, which is so admirably suited for termination of the titration at the equivalence point.

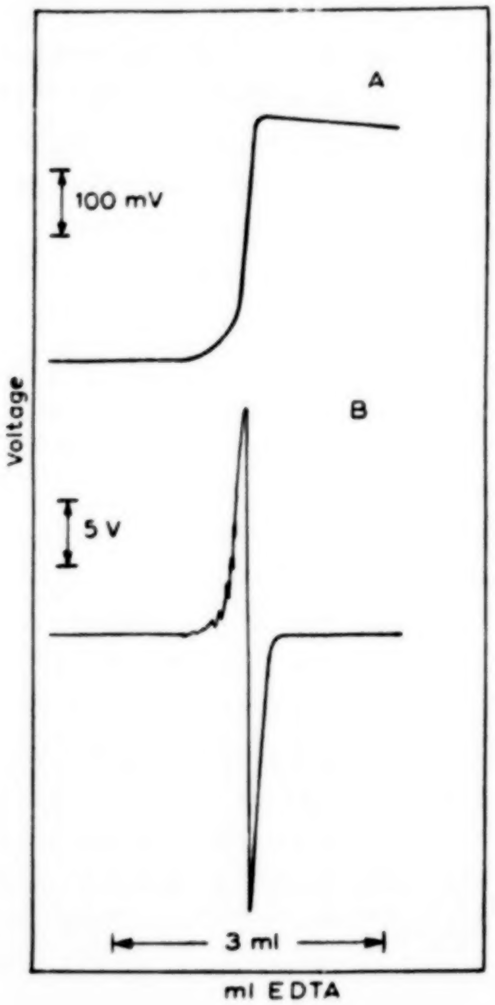

Fig. 1. Recorded curves for the automatic titration of calcium with EDTA. A. Ordinary titration curve from output of detector circuit. B. Electronically computed second-derivative curve from output of amplifier-derivative circuit, which is fed to the relay system for automatic end-point termination.

The difference of the stability constants for Mg–EBT and Mg–EDTA is not large, $10^{7.0}$ and $10^{8.7}$, respectively, and the rate of absorbance change at the end-point for the titration of both calcium and magnesium at pH 10 is not as great as for the titration of calcium using calcon indicator. However, the end-point is sharp enough to provide a good derivative signal that terminates the titration exactly at the equivalence point, again using a titrant flow rate of 3 ml/min. Some authors[3] have suggested heating the solution to 45° and titrating the heated solution in order to increase the sharpness of the end-point, but this does not seem necessary for the automatic derivative titrations, probably because of the very efficient stirring.

There is the possibility of coprecipitation of some calcium when titrating the calcium in the presence of large amounts of magnesium hydroxide, but this was found to be insignificant for any practical samples of dolomite or limestone. The coprecipitation was significant when the weight ratio of magnesium to calcium was much greater than one to one.

The high pH at which the calcium titration is performed assures the quantitative precipitation of magnesium as magnesium hydroxide, and the calcium can be selectively titrated. There is the possibility of some calcium hydroxide precipitation at the high pH used, but this would go back into solution as the titration progresses.

The amount of magnesium hydroxide precipitated and dispersed throughout the solution varies from sample to sample, causing different light scattering and different light intensities reaching the detector at the end-point for the calcium titration. However, this does not affect the titration results by the derivative technique because the electronic derivative system can determine the sharp inflection at the end-point, as long as there is sufficient light reaching the detector.

The 650-mμ filter is the most suitable to use for both the EBT and calcon indicators because at this wavelength there is a large difference in absorptivity of the metal ion–indicator complex and the free indicator, and the filter provides a wavelength band where the sensitivities of the detector and light source are sufficient to provide a good output signal to the control unit. At this preselected wavelength, both indicators provide absorbance increases at the end-points.

Ions which interfere in the usual titration of calcium and magnesium using EBT indicator also interfere in the titration of calcium with calcon. However, it is possible to easily prevent interferences by the ions probable in dolomites and limestones. Various metal ions and phosphates are precipitated with the R_2O_3 group, but traces of iron, aluminium, manganese and titanium escape the precipitation, and because they can block both indicators, it is necessary to mask them. This can be done effectively by adding a few drops of triethanolamine[14,15], after iron(III) has been first reduced with ascorbic acid. Cyanide has also been used as a masking agent[16] and hydroxylamine hydrochloride for the reduction of iron(III). Barium and strontium can be titrated with calcium and cause a positive error. This error is not significant, however, because these elements are rarely present in significant quantities in limestones and dolomites. Barium interference can be eliminated by addition of sulfate ions to the solution prior to addition of sodium hydroxide.

PROCEDURE

Preparation of automatic titrator

The "Spectro-Electro" titrator is switched to the "Spectro" position; the polarity switch thrown to position 2; the filter wheel turned to the 650 mμ position; the pegs in the base set to properly position the 50-ml beakers; the small stirrer, delivery tip, and suitable buret connected; and the titrant delivery rate set at about 3 ml/min. The same conditions are suitable for both end-points.

Standardization of titrant

The 0.01 M EDTA titrant is readily standardized. Pipet a 5-ml aliquot of standard calcium carbonate into a 50-ml beaker, dilute to about 25 ml with distilled water, add enough sodium hydroxide to adjust pH to 12.5–13 (about 2.5 ml of 1 N NaOH, test with pH paper), add one or two drops of calcon indicator, insert beaker in automatic "spectro" titrator, push start button to start stirring and delivery of titrant and read buret after automatic termination at the end-point.

Preparation of dolomite and limestone samples

Weigh 1.000 g of a representative sample into a 250-ml beaker and add cautiously, to avoid loss by evolution of CO_2, a mixture of 15 ml perchloric acid (70%) and 15 ml water[17]. The beaker should be covered with a cover-glass and the contents evaporated on a sandbath until the solution becomes colorless (the time required varies depending on the composition of the sample, the maximum being about 2 h in case of samples rich in silica).

The beaker is then removed from the sandbath, the solution diluted four fold with water, heated to boiling and the silica filtered off and washed with dilute hydrochloric acid. If the residue is appreciable, the paper is ignited and the residue fused with sodium carbonate. The fusion mixture is dissolved in hydrochloric acid (1 : 1), filtered, and washed and the filtrate is added to the original filtrate.

The combined filtrates are heated nearly to the boiling point and the solution is then made alkaline with NH_4OH (pH 6–7) to precipitate the R_2O_3 and the filtrate is diluted to the mark in a 500-ml volumetric flask. If the R_2O_3 precipitate is large, it carries down some calcium and magnesium; in such cases the precipitate is redissolved in HCl and the R_2O_3 reprecipitated.

Titration of total calcium and magnesium

Pipet a 5-ml aliquot of the prepared sample into a 50-ml beaker and dilute up to 25 ml with distilled water. Add 2 ml of the ammonium chloride–ammonium hydroxide buffer and a few drops of triethanolamine, insert beaker into titrator and start the stirrer to thoroughly mix masking agent with sample. Then add 2 drops of the Eriochrome Black T indicator solution and titrate by pushing the start button on the derivative control unit. The buret is read after automatic termination at the end-point.

The color change is usually from wine-red to blue; but in cases of iron in the solution, the final color may be green-blue.

Titration of calcium

Another 5-ml aliquot of the prepared sample is added into a 50-ml beaker and diluted up to 25 ml with distilled water. A small amount of ascorbic acid is added and the solution is heated to about 40–50°. 1*N* NaOH is added to bring the pH of the solution at 13 (use pHydrion paper). A few drops of triethanolamine are added, the beaker is inserted-in the automatic titrator, and the stirring is started. One drop of the calcon indicator solution is then added, the start button on the titrator pressed and the sample automatically titrated with standard EDTA solution. The color change is from pink to blue. One ml of 0.01000*M* EDTA solution is equivalent to 0.4008 mg of calcium or 0.5608 mg of CaO.

Magnesium

Magnesium is calculated using the volume obtained by subtracting the volume of EDTA used for the calcium titration from the volume used in the total calcium and magnesium titration. 1 ml 0.01000*M* EDTA solution is equivalent to 0.2432 mg magnesium or 0.4032 mg MgO.

CALCULATIONS

The percentages of calcium and magnesium oxides can be rapidly calculated by equations (1) and (2), respectively, if 1.000 g of sample is weighed, prepared, made up to volume in a 500-ml volumetric flask, and a 5-ml aliquot taken for titration.

$$A \times B \times 10 = \%\,\mathrm{CaO} \qquad (1)$$

$$C \times (D - B) \times 10 = \%\,\mathrm{MgO} \qquad (2)$$

where,

A = mg of calcium oxide per ml of EDTA solution

B = ml of EDTA solution used in titration, with calcon as indicator

C = mg of magnesium oxide per ml of EDTA solution

D = ml of EDTA solution used in titration, with Eriochrome Black T as indicator.

RESULTS AND DISCUSSION

Hundreds of samples containing known concentrations of calcium and magnesium in different amounts and in different ratios, were titrated to check the proposed method. Some representative data are shown in Table I. The calcium error was always about ± 0.1%, except in cases where the ratio of magnesium to calcium was greater than one. In these cases the results for calcium were lower because of some coprecipitation of calcium as illustrated by sample 6 in Table I.

The results for magnesium were as accurate and reproducible as the results for calcium when the volume of EDTA involved in the calculation for magnesium was several ml. In cases where this volume was very small, the relative error increased because of the buret-reading errors, as illustrated by several results for low con-

TABLE I

AUTOMATIC TITRATION RESULTS FOR SAMPLES CONTAINING KNOWN AMOUNTS OF CALCIUM AND MAGNESIUM

Sample No.	Calcium		Magnesium	
	Taken, mg	*Found, mg*	*Taken, mg*	*Found, mg*
1	1.202	1.203	—	—
2	1.202	1.202	0.246	0.248
3	1.202	1.204	0.493	0.493
4	1.202	1.203	0.739	0.739
5	1.202	1.199	1.231	1.230
6	1.202	1.190	1.970	1.975
7	4.008	4.010	—	—
8	4.008	4.006	0.177	0.185
9	4.008	4.009	0.246	0.252
10	4.008	4.009	0.493	0.497
11	4.008	4.012	1.231	1.228

centrations of magnesium in Table I. Smaller errors for low concentrations of magnesium are possible by using a buret with smaller reading error.

The results for the analysis of National Bureau of Standards dolomite 88 and limestone 1a are given in Table II. Corrections were made in order to account for the titration of strontium with EDTA. The maximum deviation from the average for the determination of calcium oxide was 0.10% and of magnesium oxide 0.03%.

The digestion of the samples can also be done by the hydrochloric acid procedure; however, the perchloric acid method is equally accurate and more rapid because of elimination of a required evaporation to dryness and double dehydration[17].

Larger aliquots of sample can be taken for titration in larger beakers. A 5-ml aliquot is recommended in the proposed procedure because of the smaller quantities of reagents and titrant consumed and shorter titration time. The obtained results are accurate within 0.1% as shown in Table II.

TABLE II

AUTOMATIC TITRATION RESULTS FOR CALCIUM AND MAGNESIUM IN NBS DOLOMITE AND LIMESTONE SAMPLES

Sample No.		CaO %			Mg %	
		EDTA value	*Reported value*		*EDTA value*	*Reported value*
NBS dolomite 88		30.49			21.45	
		30.46			21.42	
		30.43			21.40	
		30.40			21.39	
		30.52			21.43	
	av.	30.46	30.49	av.	21.42	21.48
	av. dev.	0.04		av. dev.	0.02	
NBS limestone 1a						
		41.38			2.20	
		41.40			2.14	
		41.25			2.17	
		41.27			2.14	
		41.20			2.20	
	av.	41.30	41.32	av.	2.17	2.19
	av. dev.	0.07		av. dev.	0.02	

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SUMMARY

A direct automatic derivative spectrophotometric EDTA titration procedure for determination of calcium and magnesium in Dolomites and Limestones is described. Calcium is automatically titrated in the presence of magnesium at pH 13 using Calcon as indicator, and the total amount of calcium and magnesium at pH 10 using Eriochrome Black T as indicator. The method is simple, precise and accurate, and requires less than 5 min for both titrations. The subjective evaluation of end-points is eliminated and the attention of the operator is not required because the titrations are automatically terminated at the end-point.

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Received April 8th, 1958

DETERMINATION OF COPPER, LEAD, TIN AND ANTIMONY BY CONTROLLED-POTENTIAL ELECTROLYSIS

III. ADAPTATION OF THE METHOD TO THE ANALYSIS OF SOME ALLOYS

by

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In a previous paper the author has described a general method utilizing controlled-potential electrolysis for the successive determination of copper, lead, tin and antimony[1].

A second paper described the application of this method to the analysis of bronzes and brasses[2], but also other alloys may be analysed by modifying the procedure of the general method to suit each special case.

In the present work the special rules to be followed and data necessary for the analysis of some alloys are outlined. The general method and the equipment needed have been described in the two previously published papers[1,2].

ANALYSIS OF TIN-BASE BEARING ALLOYS

As shown in Table I, the previously described method is suitable for the determination of copper and lead present in this type of alloys. Treat 1 or 2 g of alloy in a 400-ml tall-form beaker covered with a large-size watch glass, with 20 ml of HCl(1 + 1); heat and, as the dissolution progresses, add 1 to 2 ml of conc. HNO_3 little by little.

When the sample is entirely dissolved, dilute the solution to about 40 ml with distilled water. If any cloudiness appears on account of tin or antimony, add a few drops of conc. HCl; cloudiness will disappear upon heating. Boil the solution for a few minutes, allow to cool down to 40°–50°, add 5 g of tartaric acid dissolved in a little distilled water, wash the watch glass and beaker walls with distilled water, add to the solution 1 g of urea, 2 g of succinic acid, 2 g of hydrazine dihydrochloride, then ammonia up to a pH of about 5. Next, proceed as described previously[1]. A too high pH may be adjusted with diluted HCl.

TABLE I

ANALYSIS OF TIN-BASE BEARING METAL

Sample	*No.*	*Weight* *g*	*Results* *Cu*	*Pb*
N. 54 c Tin-base bearing metal (N.B.S.)	1	1	4.33	1.97
Cu = 4.30 Ag = 0.020 As = 0.049	2	1	4.31	1.97
Pb = 1.99 Bi = 0.028 Fe = 0.033	3	2	4.32	2.00
Sn = 86.29 Sb = 7.28 Ni = 0.012	4	2	4.34	1.97

Copper begins to deposit at —0.35 V *vs.* S.C.E. and finishes depositing at —0.40 V *vs.* S.C.E.; lead starts depositing at —0.58 to —0.60 V *vs.* S.C.E., the control potential then being very gradually brought to —0.65 V *vs.* S.C.E. because otherwise, owing to the presence of a large amount of tin and antimony, these metals may partially co-deposit; should this occur as electrolysis proceeds the current intensity will increase instead of decreasing.

Separation of copper from a hydrochloric or hydrochloric–tartaric solution

Both when working with 1 or 2 g of alloy, lead — if present in amounts greater than 150–160 mg — will precipitate as a tartrate when the electro-deposition of copper comes to an end. In this case copper may be separated from the hydrochloric solution (as obtained after sample dissolution) to which 2 g of hydrazine dihydrochloride have been added.

Copper deposits at —0.35 V *vs.* S.C.E. but, initially, such a high negative potential cannot be used unless the amount of copper is small. The electro-deposition is at first rather difficult and calls for a lot of skill and experience on the part of the operator. The author believes that the best procedure, at least with the electrodes he has used[1], is to start the electrolysis, without stirring the solution, with a current intensity ranging from 1–2 A, to which a cathode potential between —0.1 and —0.2 V *vs.* S.C.E. corresponds. Then (with the cathode potential kept constant) brief stirring periods are alternated with periods of unstirred deposition until the cathode is coated with a uniform copper plating. After this, slow stirring is maintained, which must then be gradually accelerated.

The electrolysis then follows a normal course and the cathode potential may be gradually brought first to —0.30 V *vs.* S.C.E. and later to —0.35 V *vs.* S.C.E.

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By proceeding as outlined above, it will be possible to deposit up to one g of copper.

After copper deposition, add 5 g of tartaric acid to the solution and adjust the pH with ammonia to 5–5.3; however, if the tin present exceeds 30–40 mg a precipitate will form on account of the bivalent tin developed during electrolysis.

This trouble may be remedied in two ways:

(A) by passing a stream of oxygen through the solution for 10–15 min before or after the addition of tartaric acid;

(B) by adding the tartaric acid to the cold solution before copper electrolysis, which is not at all affected by the presence of this acid. This remedy is undoubtedly the best of the two because it is more rapid and just as efficient.

Whichever one is chosen, the only precipitate that may form during the addition of ammonia, if less than 400 mg zinc is present, is lead tartrate, which will, however, re-dissolve during lead electrolysis.

Subsequently tin and antimony are deposited, as described in the general method[1]. The absence of antimony, however, is preferable because small amounts of it sometimes deposit with copper from the hydrochloric or hydrochloric–tartrate solution. With regard to this, the reader is referred to the information given in the last part of the discussion of the general method[1].

ANALYSIS OF LEADED BRONZE

The above-mentioned procedure is particularly suitable for the analysis of leaded bronze which, apart from copper and small amounts of tin, contains up to 25% of lead.

Dissolve 1 g of alloy in a flask equipped with a condenser, using 15 ml of HCl (1 + 1) and a 36% H_2O_2 solution, as described previously[1].

To dissolve all the lead present, numerous additions of hydrogen peroxide are necessary.

After boiling off the excess hydrogen peroxide and after washing the condenser with distilled water transfer the contents of the flask to a 400-ml tall-form beaker, using distilled water as a washing solution, and add 2 g of hydrazine dihydrochloride. At this point the operator may proceed in one of the two following ways:

(A) deposit copper at —0.35 V *vs.* S.C.E., add 5 g of tartaric acid, then conc. NH_3 up to a pH of 5.2 and deposit the lead;

(B) add 5 g of tartaric acid and deposit copper at —0.35 V *vs.* S.C.E.; add NH_3 up to a pH of 5.2 and deposit the lead.

In both cases the addition of ammonia causes the precipitation of lead as a tartrate. Lead is electrolysed in the presence of the precipitate and deposited on the copper-plated cathode or directly on the platinum cathode (the deposit is then removed with HNO_3, 1 + 1), provided an initial current intensity of 0.1 A is not exceeded; 5–10 min after complete dissolution of the precipitate set the cathode potential at —0.60 V *vs.* S.C.E., and continue the electro-deposition from —0.60 to —0.65 V *vs.* S.C.E. in accordance with the general method[1].

Tin, if present, is deposited as described in the general method.

Table II shows the results obtained with synthetic solutions of leaded bronze obtained by dissolving weighed quantities of the pure metals with 15 ml of HCl(1 + 1) and hydrogen peroxide.

TABLE II

ANALYSIS OF SYNTHETIC SOLUTIONS OF LEADED BRONZE
(All weights in g)

No.	Cu		Pb		Sn	
	Weighed	*Found*	*Weighed*	*Found*	*Weighed*	*Found*
1	0.7954	0.7960	0.2022	0.2020	0.0104	0.0099
2	0.7388	0.7382	0.2391	0.2390	0.0062	0.0058
3	0.7050	0.7055	0.2026	0.2028	0.0136	0.0128
4	0.7617	0.7614	0.2368	0.2370	0.0067	0.0064
5	0.7605	0.7598	0.2456	0.2460	0.0048	0.0044
6	0.7558	0.7554	0.2490	0.2494	0.0044	0.0044
7	0.8369	0.8364	0.1736	0.1734	0.0043	0.0038
8	0.7552	0.7548	0.2490	0.2482	0.0050	0.0049

Tests 1–2 = Tartaric acid added after copper deposition.
Tests 3–8 = Tartaric acid added before copper deposition.

ANALYSIS OF Ag–Cu–Cd–Zn ALLOYS

In a 400-ml tall-form electrolysis beaker dissolve 1 g of alloy with 10 ml of HNO_3 (1+1) and heat moderately if required. When dissolution of sample is completed, wash the watch glass and beaker walls with distilled water, add 10 ml of a 60% $HClO_4$ solution and heat to white fumes. Allow to cool off a bit, wash the beaker walls with distilled water and again heat to white fumes. Allow to cool once more, dilute to approximately 50 ml with distilled water and boil for a few minutes; immediately add 1 g of urea and dilute to 200–250 ml.

If the calomel electrode is immersed in this solution, it will hardly be possible to avoid the precipitation of silver chloride; but to deposit silver a rigorous check of the cathode potential is not essential; it will suffice to adjust the total potential applied at the electrodes by means of the variac or of the potentiometric resistor, depending on whether automatic or manual apparatus is used.

For the electro-deposition of silver the overall potential applied to the electrolysis cell must not exceed 1.5 V, but, initially, it is advisable to remain under 1.3 V so that current intensity will be about 0.3–0.4 A; when most of the silver has deposited the potential tends to rise but it may nevertheless be kept within 1.3–1.5 V by suitable manipulation of the variac or the resistor.

Once electrolysis is finished, the total potential no longer tends to vary; it is then brought to 1.5 V and kept at this value for a few minutes; in this way, the operator may be sure that silver has deposited completely.

At this point, no cloudiness must develop upon immersion of the calomel electrode; the cathode potential must not be less than +0.1, or at the most, +0.05 V *vs.* S.C.E. Wash, dry and weigh in the usual manner.

Next, deposit copper at an initial cathode potential of —0.05 to —0.1 V *vs.* S.C.E., which is then gradually brought to —0.3 V *vs.* S.C.E. When current intensity drops to 0.1 A it becomes useless to maintain cathode potential at a constant value since, even without any further adjustment, values so negative as to permit the deposition of cadmium are never reached.

After copper has deposited, add to the solution 10 g of tartaric acid, 2 g of hydrazine dihydrochloride and then ammonia up to a pH of 6.8–7.2.

Check the pH of the solution using narrow-range test papers and if necessary correct by adding hydrochloric acid and ammonia. The degree of accuracy need not be perfect because the entire pH range between 6.5 and 8 is suitable for cadmium deposition. During neutralization, a precipitate may form but it will re-dissolve at the indicated pH value.

The resulting buffer capacity of the solution is not high and, if cadmium exceeds 0.3 g, a periodic check with the narrow-range pH test papers will be required during electrolysis; the pH must be adjusted by a few drops of ammonia or else the solution will become more acid and precipitates will form.

If more than 0.4-0.5 g of zinc are present the solution must not be brought to a pH higher than 6.8 because at 7.2 the solution becomes slightly cloudy. In an attempt to obtain a solution with a higher buffer capacity the author tried replacing tartaric acid ($pK_1 = 3$; $pK_2 = 4.5$) by citric acid ($pK_1 = 3.1$; $pK_2 = 4.8$; $pK_3 = 6.7$). This did improve the buffer capacity, but not all the cadmium could be deposited; instead, even up to 1 g of zinc was quantitively deposited.

Finally, add to the electrolysis solution 10 ml of a freshly prepared 0.2% gelatin solution; cadmium deposits very nicely even in the absence of gelatin but the latter significantly improves the successive deposition of zinc.

Most of the cadmium deposits in the —0.8 to —0.9 V *vs.* S.C.E. range but for complete deposition the cathode potential is brought gradually to —1 V *vs.* S.C.E.

After the removal of cadmium, add 15 ml of concentrated ammonia to the solution and deposit the zinc, starting to electrolyse at —1.4 and then increasing to —1.45 V *vs.* S.C.E.

If manual apparatus is used, no adjustment is made of the cathode potential, which during electrolysis spontaneously becomes more negative, dropping from —1.4 to —1.5 V *vs.* S.C.E. If for any reason whatsoever the cathode potential does not drop naturally to this value it must be adjusted to —1.5 V *vs.* S.C.E. 15-20 min after the beginning of electrolysis. On the other hand, however, towards the end of electrolysis the cathode potential frequently shows a tendency to drop to —1.6 or —1.7 V *vs.* S.C.E.; but if the best possible deposit is sought, the potential should never be allowed to fall to these exceedingly negative values and should be kept constant at —1.50 V *vs.* S.C.E. until the current intensity has decreased to less than 0.20-0.15 A; after this time the cathode potential need no longer be kept under control or, at the most, it may be brought to —1.55 V *vs.* S.C.E.

When the amounts of zinc being deposited are small, it often happens that in limiting the cathode potential the predominant reaction is the development of hydrogen, a factor that keeps current intensity at a high value throughout the deposition.

Once some experience in zinc deposition has been acquired by the operator, handling the electrolysis of zinc becomes even simpler than for the other metals inasmuch as it demands less control of cathode potential.

The deposits of all four metals show optimum clinging and appearance characteristics. Each metal may be deposited on the coating of the preceding one or directly on platinum; zinc should preferably be deposited on cadmium or copper, because sometimes the platinum net blackens after dissolution of zinc by an acid, thus requiring calcination to eliminate the zinc that has alloyed with the platinum.

The deposition of each metal takes from 45-60 min.

Table III shows the optimum results obtained with synthetic solutions prepared by dissolving the pure metals in nitric acid (1+1) and bringing twice to white fumes of perchloric acid; when only cadmium and zinc are present, the two metals are dissolved directly in 10 ml of a 60% perchloric acid solution, by heating to white fumes and boiling the perchloric acid.

TABLE III

ANALYSIS OF SYNTHETIC SOLUTIONS OF Ag–Cu–Cd–Zn
(All weights in g)

No.	*Ag*		*Cu*		*Cd*		*Zn*	
	Weighed	*Found*	*Weighed*	*Found*	*Weighed*	*Found*	*Weighed*	*Found*
1	0.4996	0.4993	0.1450	0.1447	0.1788	0.1784	0.1288	0.1290
2	0.4990	0.4988	0.1604	0.1602	0.2117	0.2117	0.2052	0.2054
3	0.4295	0.4292	0.1030	0.1028	0.1080	0.1080	0.3967	0.3964
4	0.6079	0.6076	0.3058	0.3055	0.3090	0.3086	0.4917	0.4920
5	1.0026	1.0024	1.0026	1.0029	0.4993	0.4991	0.4894	0.4896
6	—	—	—	—	0.5075	0.5072	0.0046	0.0050
7	—	—	—	—	0.5055	0.5050	0.0065	0.0070
8	—	—	—	—	0.4975	0.4977	0.0068	0.0070
9	—	—	—	—	0.0065	0.0060	0.4990	0.4987
10	—	—	—	—	0.0087	0.0082	0.4966	0.4970

Tests 1–4: each metal deposited on platinum.
Test 5 : Ag deposited on Pt; Cu on Ag; Cd on Cu; Zn on Cd.
Tests 6–8: Cd deposited on Pt; Zn on Cd.
Tests 9–10: Cd deposited on copper-plated gauze; Zn on Cd.

The methods generally used to analyse these metals are long and rather difficult processes[3]. The methods based principally on constant-intensity electrolysis[4] are also very time-consuming. A much more rapid method is one that utilizes constant total potential electrolysis to deposit silver, copper and cadmium from a solution acidified with perchloric acid and constant-intensity electrolysis to deposit zinc from an alkaline solution[5]. However, it has been noticed that the deposition of cadmium from an acid solution is often incomplete, while the deposition of zinc — performed at a constant intensity from an alkaline solution — gives almost consistently high results and becomes very difficult when the amount of zinc present exceeds 0.15–0.20 g. Controlled-potential electrolysis has been employed to deposit silver[6] and, successively, copper[7]. The procedure is as follows: electrolyse the ammoniacal solution and pass a gaseous stream through the solution during both depositions, oxygen for silver and nitrogen for copper. The presence of nitrates in the solution makes it impossible to deposit cadmium and zinc from it.

The method proposed by the author has remarkable advantages compared to the preceding ones, because it requires less time and has greater accuracy as well; strong variations in the percentages of the four elements do not impair the efficiency of the method.

ANALYSIS OF COPPER-CADMIUM ALLOYS

On account of the small amounts of cadmium (1–1.5%) present in the alloys of this type that are examined in our laboratories, a 1-g sample is used.

After what has been said with regard to the analyses of the previous alloys, it is evident that the analysis of the copper–cadmium alloys may be carried out in one of the following ways:

(a) dissolution of the alloy with 10 ml of HCl(1+1) and 36% H_2O_2, deposition of copper from a tartaric-ammoniacal solution as for bronzes[2]; after removal of copper the pH of the solution is adjusted to 6.8-7.2 with ammonia and the cadmium is deposited on the previous copper coating or directly on platinum at a cathode potential of from —0.85 to —0.95 V *vs.* S.C.E.

(b) dissolution same as in (a), deposition of the copper from a hydrochloric solution same as described for leaded bronze; next, addition of 5 g of tartaric acid, 2 g of hydrazine dihydrochloride, adjustment of the pH to 6.8-7.2 with ammonia and deposition of cadmium.

(c) same as outlined for the deposition of copper and cadmium in the Ag-Cu-Cd-Zn alloys.

TABLE IV

ANALYSIS OF SYNTHETIC SOLUTIONS OF Cu-Cd
(All weights in g)

No.	*Procedure*	*Cu*		*Cd*	
		Weighed	*Found*	*Weighed*	*Found*
1	a	0.9943	0.9937	0.0057	0.0053
2	a	1.0426	1.0418	0.0088	0.0084
3	a	1.0050	1.0045	0.0163	0.0158
4	a	1.0064	1.0058	0.0302	0.0296
5	b	1.0155	1.0152	0.0085	0.0081
6	b	1.0045	1.0040	0.0115	0.0117
7	b	1.0214	1.0212	0.0135	0.0131
8	b	1.0120	1.0117	0.0196	0.0194
9	b	1.0060	1.0058	0.0215	0.0214
10	b	1.0081	1.0076	0.0090	0.0090
11	b	1.0082	1.0082	0.0046	0.0044
12	b	1.0113	1.0114	0.0050	0.0048

Procedures (a) and (c) require the same time for the deposition of the two metals, but the dissolution of the sample is more rapid with the former; in procedure (b) the deposition of large amounts of copper from a hydrochloric solution is rather troublesome. Table IV indicates some results obtained when analysing synthetic solutions according to procedures (a) and (b).

SUMMARY

Some modifications of a previous method are described here, whereby it is possible to analyse tin-base bearing alloys, leaded bronze, silver solders and copper-cadmium alloys, by controlled-potential electrolysis.

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Received April 21st, 1958

DETERMINATION OF URANIUM BY CUPFERRON WITH COMPLEXONE III AS THE MASKING AGENT

by

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In previous communications dealing with complexone III as a masking agent and cupferron as a precipitant it was shown that both tetra- and hexavalent uranium interfere in the determination of titanium[1] and niobium[2]. Therefore it was considered worthwhile to study the applicability of cupferron as a reagent for hexavalent uranium. This reagent was previously used for the precipitation of tetravalent uranium from an acid solution[3].

From a solution maintained at a pH between 6 and 7 by ammonium acetate–acetic acid buffer, hexavalent uranium is separated by the reagent from the following ions: copper, bismuth, ferric, chromium, thorium, aluminium, molybdate, vanadate and tungstate, which are kept in solution by complexone III. The ions of cadmium, lead, zinc, manganese, nickel, cobalt, rare earths, alkalis and alkaline earths have no effect but the ions of titanium, beryllium, tin (stannous and stannic), antimony, arsenic and phosphate interfere. The uranium–cupferron complex like other metal–cupferron complexes can be ignited to oxide before weighing.

EXPERIMENTAL

Reagents and standard solutions

A 5% aqueous solution of cupferron was prepared from E. Merck's (*pro-analysi*) sample.

A standard solution of hexavalent uranium was obtained from uranyl nitrate and its strength as U_3O_8 was determined by TROMBE's method[4].

Other chemicals and standard solutions used were the same as those described in the first publication of the series[1].

TABLE I

U_3O_8 taken mg	*Ions added* mg		*U_3O_8 found* mg	*U_3O_8 taken* mg	*Ions added* mg		*U_3O_8 found* mg
24.8	Cu^{+2}	250.0	25.0	24.8	Al^{+3}	137.0	24.6
49.5		500.0	49.8	49.5		274.0	49.7
24.8	Bi^{+3}	250.0	24.9	24.8	V^{+5}	174.8	25.0
49.5		500.0	49.3	49.5		281.2	49.3
24.8	Fe^{+3}	250.0	24.5	49.5	Mo^{+6}	361.0	49.5
49.5		560.0	50.0	99.0		722.0	99.5
49.5	Th^{+4}	462.8	49.6	24.8	W^{+6}	247.6	24.7
99.0		925.6	99.4	49.5		414.0	49.5
24.8	Cr^{+3}	249.6	24.6				
49.5		374.0	49.3				

Procedure

A large excess (about 10–15 times) of complexone III was added to a solution containing uranyl nitrate, either alone or admixed with other ions from which it has to be separated. The pH of the solution was then adjusted to 6–7 by the addition of a 20% ammonium acetate solution. The solution was then diluted to 250–300 ml, cooled to about 10° and mixed with the reagent solution added dropwise under vigorous stirring till the precipitation was complete. The precipitate was then filtered, washed with cold wash water containing a little cupferron, dried, ignited to U_3O_8 and weighed (*cf.* Table I).

SUMMARY

At a pH between 4 and 6, hexavalent uranium is quantitatively precipitated by cupferron in the presence of complexone III and thus can be separated from Bi^{+3}, Cu^{+2}, Fe^{+3}, Cr^{+3}, Al^{+3}, Th^{+4}, Cd^{+2}, Pb^{+2}, Zn^{+2}, Mn^{+2}, Ni^{+2}, Co^{+2}, alkali metals, alkaline earth metals, rare earth metals, VO_3^- MoO_4^{-2} and WO_4^{-2}.

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Received March 31st, 1958

SOLUBILITÉ DE L'ACIDE ÉTHYLÈNEDIAMINOTÉTRAACÉTIQUE (COMPLEXON II) EN FONCTION DU pH

TITRAGE AMPÉROMÉTRIQUE DU COMPLEXON

par

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BUT DU TRAVAIL

L'étude de la solubilité du complexon II en fonction du pH permet de calculer la quantité maximum d'ions complexables à un pH déterminé[1]; de plus, son utilisation peut être d'une aide précieuse pour certaines séparations délicates telles que celles des terres rares[2]. L'exemple de la séparation de l'yttrium et de l'europium est particulièrement frappant: à pH 3.5 il n'y a pratiquement pas de séparation, à pH 3.1 elle est excellente.

Les titrations par le complexon se font généralement à l'aide d'un indicateur coloré donnant des réactions caractéristiques en présence de certains ions métalliques. Cet indicateur peut être remplacé par une mesure de point d'équivalence au moyen d'appareils optiques tels que le spectrophotomètre ou d'appareils électriques tels que le pH mètre, le potentiomètre ou le polarographe.

La détermination du complexon peut évidemment se faire par le processus inverse. De nombreux titrages se font, en effet, en retour à l'aide d'un cation fortement complexé[3–9].

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Il faut de même, lors de la préparation d'une solution de complexon, la standardiser par titration.

Plusieurs auteurs[10–13] ont d'ailleurs mis au point différents procédés de détermination directe du complexon. Certains envisagent le problème sous une forme cinétique et étudient les relations liant le pH à la vitesse de formation du complexe pendant la titration[14].

Nous avons choisi, de préférence à toute autre méthode, le titrage ampérométrique du complexon par le zinc en tampon ammoniacal. L'onde polarographique du zinc dans ce milieu, est très bien définie et d'autre part, la stabilité du complexe obtenu est très grande. La méthode est rapide, précise et ne nécessite pas l'emploi d'un indicateur coloré.

PARTIE EXPÉRIMENTALE

Le polarographe utilisé est un ,,Sargent'' modèle XXI équipé d'un statif pour électrodes ,,Radiometer''. Les dosages se faisant par étalonnage et non de manière absolue, la constante capillaire n'a pas été déterminée. Il suffit de vérifier la constance de *t*, durée de vie de la goutte de mercure.

La solution étalon de zinc, préparée à partir de zinc métallique 99.99, a la composition suivante:

Zn^{+2}	$10^{-3}M$
NH_4Cl	$1M$
NH_4OH	$1M$
Na_2SO_3	$10^{-1}M$
gélatine	0.01%

Le sulfite de sodium a été ajouté en quantité suffisante pour éliminer l'oxygène dissous; la concentration en gélatine est celle couramment utilisée pour supprimer le maximum de l'onde du zinc.

Neuf solutions saturées de complexon ont été préparées et ajustées à des pH compris entre 1.13 et 7.32 par addition d'acide chlorhydrique ou d'ammoniaque. Ces pH ont été mesurés avec le pH-mètre Radiometer 3. Les solutions saturées de complexon ont ensuite été diluées avec un tampon ammoniacal de composition identique à celle de l'étalon, mais ne comprenant pas de zinc. Les titrages ont été effectués en ajoutant à une quantité toujours identique (10 ml) de la solution étalon de zinc, les différentes solutions diluées de complexon.

Le Tableau I donne, pour chaque solution de complexon, son pH, la quantité utilisée pour complexer la totalité du zinc ainsi que les concentrations correspondantes des solutions saturées.

TABLEAU I

Solution	*pH*	*Quantité nécessaire*	*Solution diluée*	*Concentration M*	*Concentration en %*	*log M*
1	1.13	32.5	1/1	$3.07 \cdot 10^{-4}$	$8.6 \cdot 10^{-3}$	—3.51
2	1.97	57.6	1/1	$1.73 \cdot 10^{-4}$	$4.9 \cdot 10^{-3}$	—3.76
3	2.86	13.9	1/1	$7.18 \cdot 10^{-4}$	$20.9 \cdot 10^{-3}$	—3.14
4	3.31	3.0	1/1	$3.33 \cdot 10^{-3}$	$97.2 \cdot 10^{-3}$	—2.48
5	3.80	5.12	1/20	$3.90 \cdot 10^{-2}$	1.14	—1.41
6	4.11	4.62	1/160	$3.46 \cdot 10^{-1}$	10.10	—0.46
7	4.67	4.27	1/800	1.87	54.60	+0.27
8	6.12	6.87	1/1250	1.81	52.85	+0.26
9	7.32	4.13	1/1000	2.42	70.66	+0.38

CONCLUSIONS

L'ensemble des valeurs déterminées par titrage ampérométrique a permis le tracé de la courbe de solubilité du complexon II en fonction du pH (Fig. 1). Une anomalie se manifeste vers les pH très acides; la solubilité augmente en effet très légèrement

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en dessous de pH 2. Il est probable que la formation de certains composés d'addition tels que les chlorhydrates (puisque l'acide utilisé est l'acide chlorhydrique) justifie cette anomalie. Les amines tertiaires forment en effet facilement de tels composés, plus solubles que les amines elles-mêmes.

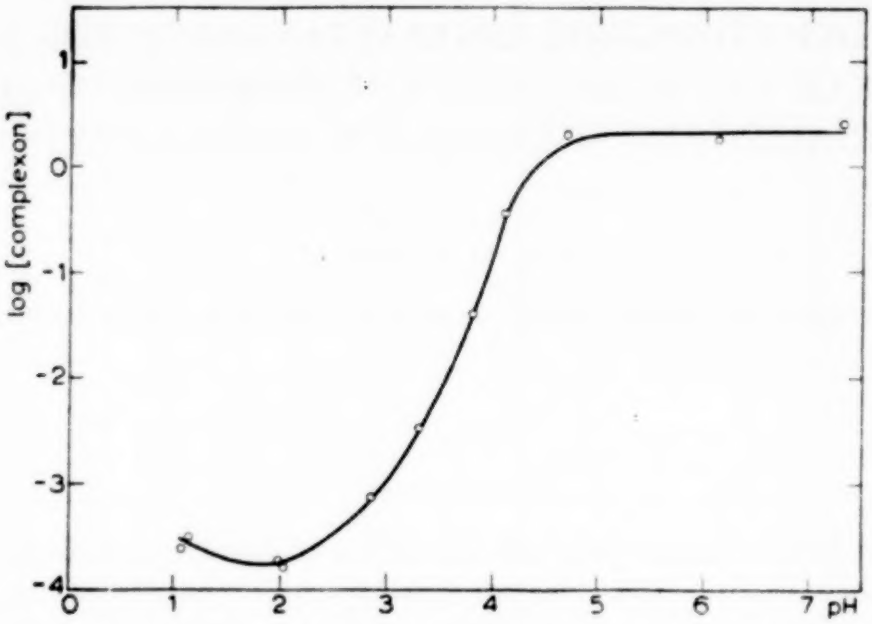

Fig. 1. Courbe de solubilité du complexon II en fonction du pH.

L'examen de la courbe montre qu'à un pH supérieur à 5, la solubilité, supérieure à 1 *M* ne varie pratiquement pas. Par contre, entre pH 2 et 5, une faible variation de pH peut soit amener une précipitation du complexon, soit permettre la complexion envisagée. Une étude plus détaillée des composés d'addition (chlorhydrates) semble offrir des possibilités d'utilisation du complexon dans le domaine des fortes acidités.

RÉSUMÉ

La comparaison des différentes méthodes de titrage du complexon II (E.D.T.A.) montre que l'ampérométrie par le zinc est rapide, précise et ne nécessite pas l'emploi d'un indicateur coloré. L'application de cette méthode a permis le tracé de la courbe de solubilité du complexon en fonction du pH.

SUMMARY

Comparison of various E.D.T.A. titration methods shows that zinc amperometry is rapid, accurate and that it is not necessary to use a coloured indicator. With this method it was possible to plot the E.D.T.A. solubility curve as a function of pH.

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Received April 8th, 1958

A SPECTROPHOTOMETRIC INVESTIGATION OF THE REACTION BETWEEN FLUORIDE AND THE COMPLEX OF SODIUM QUINALIZARIN SULPHONATE WITH ALUMINIUM

by

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INTRODUCTION

Fluoride ions bleach many coloured complexes of certain metals owing to the preferential formation of colourless complex fluorides, and most absorptiometric methods of determining fluoride rely upon this phenomenon[1-7]. It seemed possible that the complex formed between aluminium and quinalizarin[8], 1,2,5,8-tetrahydroxyanthraquinone, which is used as a spot test for aluminium[9], might be decomposed by fluoride, and that this reaction could form the basis of an absorptiometric method for determining fluorine which would be free from interference by sulphate. A disadvantage of quinalizarin is that it is almost insoluble in water and only sparingly soluble in most solvents and it is therefore generally used dissolved in concentrated sulphuric acid or in alkali hydroxide solution. This disadvantage was overcome by sulphonation of the quinalizarin in fuming sulphuric acid as described below. The water-soluble derivative obtained reacts with aluminium to form a complex which is not precipitated except in solutions of fairly high ionic strength and so no protective colloid is necessary.

EXPERIMENTAL

Apparatus

The absorbance measurements were made with a EEL Absorptiometer using 4-cm glass cells and the spectrophotometric curves were obtained from a Unicam S.P. 500 spectrophotometer using 1-cm silica cells. pH was measured with a bench-type Cambridge pH meter using a glass electrode–calomel reference electrode system.

Preparation of reagent

5 g quinalizarin, recrystallized from hot nitrobenzene, and 10 ml fuming sulphuric acid (20% SO_3) were heated to 70°–80° in a flask, the neck of which was covered to prevent absorption of moisture from the air. Sulphonation was continued for 12–24 h until a small drop of the violet liquid withdrawn on a glass rod was completely soluble in water. After cooling, the solution was poured into 200 ml distilled water, again allowed to cool, and filtered. The red filtrate was neutralized with concentrated sodium hydroxide solution to an incipient blue colour (quinalizarin acts as an acid–base indicator at pH 5–6), and was made slightly acid with dilute sulphuric acid to prevent hydrolysis of the sulphonic acid. About 4 vol. of 90% ethanol were then added with vigorous stirring to 1 vol. of the neutralized sulphonation mixture and the solution was filtered to remove precipitated sodium sulphate. The filtrate was evaporated under reduced presure to very small volume, and sodium quinalizarin sulphonate was precipitated as a red solid by adding absolute alcohol. The extinction of this substance, compared with that of purified quinalizarin, suggested that it was the disulphonate.

Spectrophotometer curves

The molar extinction curves of purified quinalizarin and sodium quinalizarin disulphonate (QAS) in 90% ethanol are shown in Fig. 1 and of aqueous QAS in an acetate buffer at pH 3.9 in Fig. 2. The increasing absorbance below 230 mμ in curve 3 is probably due to the presence of acetate ions[10].

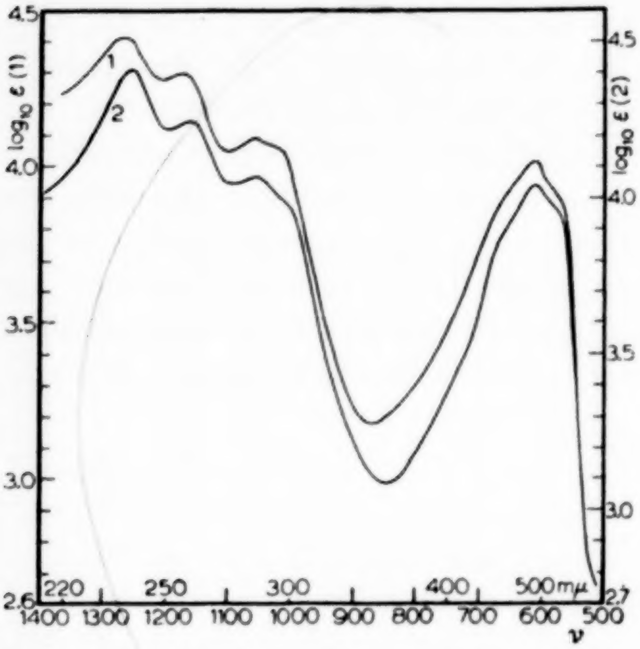

Fig. 1. Molar extinction curves of (1) quinalizarin and (2) sodium quinalizarin sulphonate in 90% ethanol.

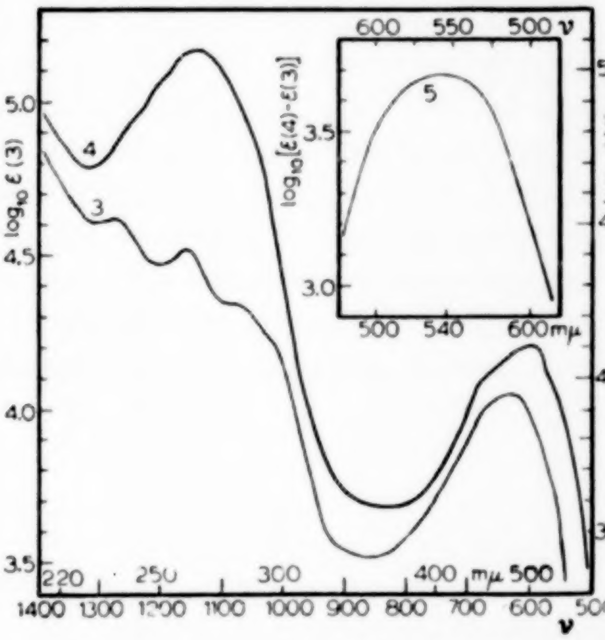

Fig. 2. Molar extinction curves of (3) sodium quinalizarin sulphonate and (4) sodium quinalizarin sulphonate and aluminium (1 Al: 2 QAS) in acetate buffer at pH 3.9. Curve 5 is the difference between 4 and 3.

The aluminium-QAS complex

The effect of adding aluminium ions to the QAS-buffer solution is shown in curve 4 of Fig. 2, the new maxima at 265 mμ and 495 mμ indicating that a complex is formed. The maximum at 265 mμ has a very strong absorbance relative to QAS but could only be used if an ultra-violet absorptiometer were available, and to develop a more generally applicable method, the maximum at 495 mμ was used to study the complex. Since QAS also exhibits a maximum fairly close to 495 mμ, the absorbance of the complex relative to a reagent blank is not necessarily greatest at this wavelength, and the difference curve 5 of Fig. 2, obtained by subtracting curve 3 from curve 4, shows that the complex has greatest absorbance relative to QAS at 540 mμ. The Ilford-605 filter provided with the EEL Absorptiometer absorbs in the neighbourhood of this wavelength and was used for the subsequent investigation.

An attempt was made to determine the ratio of aluminium to QAS in the complex using JOB's method of continuous variation[11]. This is based on the deduction that when two reactants are mixed in varying proportions such that their total concentration remains constant, the concentration of the complex formed is greatest for the mixture containing the reactants in the same relative proportions as they appear in the complex. Aluminium and QAS solutions of equal concentration, $10^{-5}M$ or $2 \cdot 10^{-5}M$, were mixed in varying proportions keeping the total volume of the mixtures constant, and the absorbance of the resultant solutions was measured relative to water at 520, 550 and 580 mμ. Since QAS has appreciable absorbance at these wavelengths, maximum absorbance does not correspond with maximum concentration of the complex. Approximate allowance was made for the absorbance of QAS by subtracting the absorbance which would have resulted if no complex had been formed; these derived quantities were plotted against the composition of the corresponding solutions. With a concentration of $10^{-5}M$, the maximum value was found for a solution containing slightly more aluminium than Al : QAS = 1, while for the concentration of $2 \cdot 10^{-5}M$, the maximum occurred for Al : QAS ratios of slightly less than unity. These observations suggested that the composition of the complex is dependent upon concentration.

There was also evidence that more than one complex was formed between aluminium and QAS. Increasing amounts of aluminium were added to solutions containing the same concentration of QAS, and the approximate spectrophotometric curves of the solutions, obtained with the EEL Absorptiometer and the Ilford filters 601–607, are shown in Fig. 3. These curves show that in addition to the maximum at about 500 mμ for an aluminium to QAS ratio of approximately unity, a second maximum at about

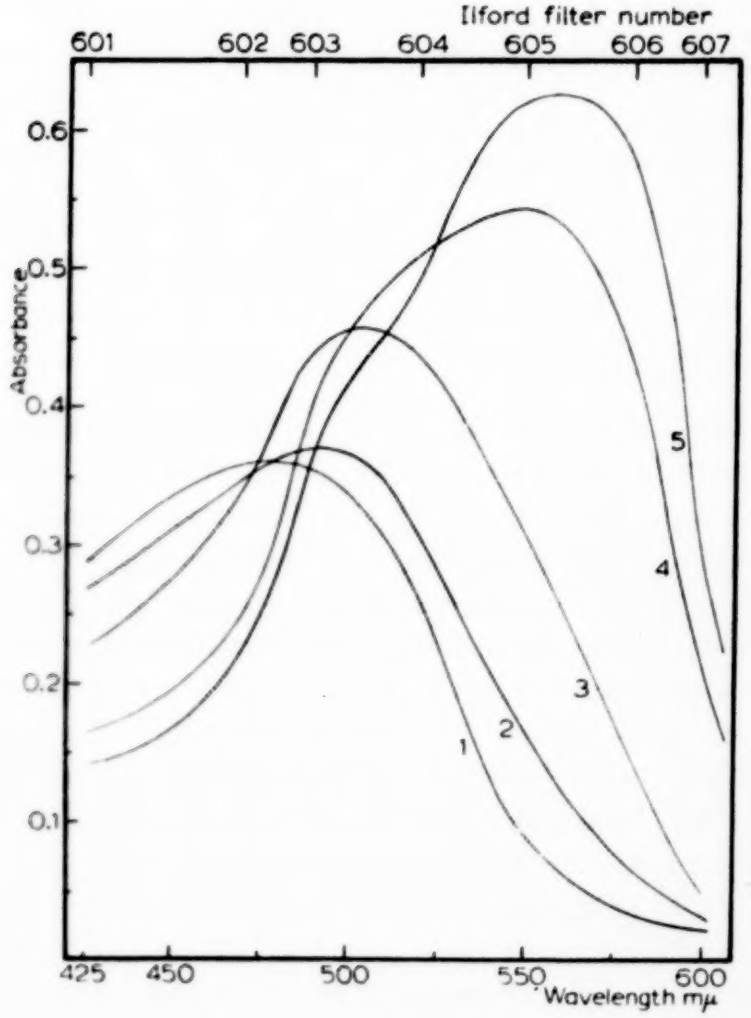

Fig. 3. Absorbance of sodium quinalizarin sulphonate in the presence of increasing quantities of aluminium. QAS concentration: $4 \cdot 10^{-6}M$. Aluminium concentration: (1) No aluminium, (2) $2 \cdot 10^{-6}M$, (3) $2 \cdot 10^{-5}M$, (4) $8 \cdot 10^{-4}M$, (5) $8 \cdot 10^{-3}M$.

570 mμ appears when the aluminium is greatly in excess of the QAS, possibly due to the formation of a complex containing aluminium to QAS in the ratio of 2 : 1 or 3 : 1.

Effect of fluoride on the aluminium-QAS complex

The bleaching action of the fluoride ion on the Al-QAS complex was investigated at several pH values. Fig. 4 shows the influence of increasing fluoride concentration on the absorbance of the complex in an 0.02*M* ammonium chloride-acetic acid buffer, the pH of which was adjusted by aqueous ammonia. The Al-QAS complex is almost completely dissociated below pH 3.4 while above pH 4, there is a loss of sensitivity to bleaching of fluoride; pH 3.9 was therefore chosen as the optimum.

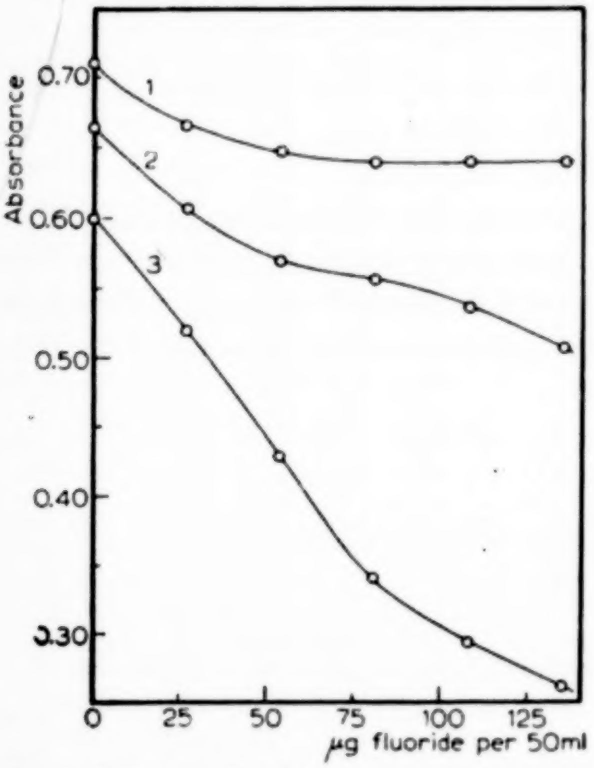

Fig. 4. Effect of fluoride on Al-QAS colour reagent at different pH; (1) pH = 4.94; (2) pH = 4.40; (3) pH = 3.96.

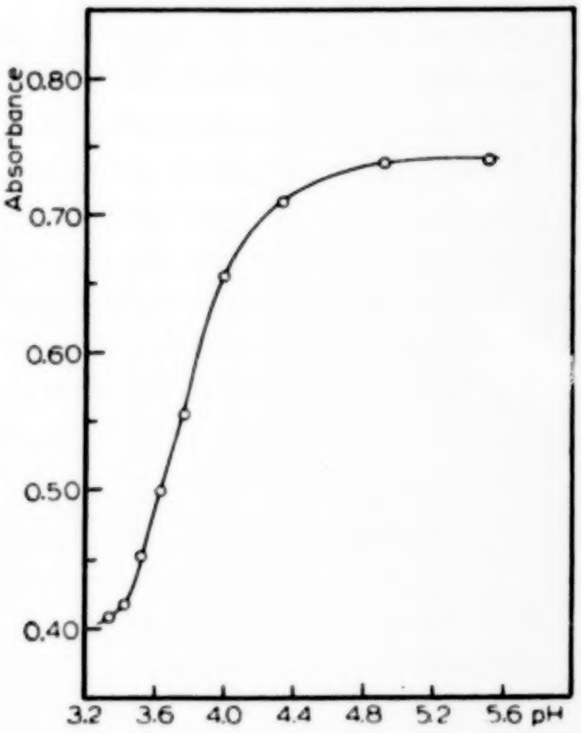

Fig. 5. Effect of pH on the absorbance of Al-QAS colour reagent.

Time of bleaching

The absorbance of a solution containing equal quantities of aluminium and QAS was measured as a function of time after adding fluoride solution. After 10 min, the reaction was 95% complete, and there was no detectable difference between the absorbance measured after 1 h and after 2 h. Measurements were therefore made 1 h after adding fluoride.

Reagents

Buffer solution. 60 ml A.R. glacial acetic acid, 25 ml A.R. hydrochloric acid (d = 1.18) and 45 ml A.R. ammonia solution (d = 0.880) were added to 800 ml distilled water. The pH was adjusted to 3.9 by further additions of ammonia and the buffer was diluted to 1 l.

QAS stock solution. 0.10 g QAS was dissolved in about 250 ml distilled water, 100 ml buffer solution added, and the solution diluted to 500 ml.

Aluminium-QAS colour reagent 4.744 g A.R. potassium alum were dissolved in 1 l distilled water;

a $4 \cdot 10^{-4}M$ solution was obtained by diluting 40 ml of this solution to 1 l. The colour reagent, prepared by mixing equal volumes of QAS stock solution and $4 \cdot 10^{-4}M$ aluminium solution, was allowed to stand for 24 h before using to allow complete development of the colour. This reagent was stable for at least one month.

Standard fluoride solution. 1.495 g sodium fluoride, recrystallized from water and dried at 105°, were dissolved in 250 ml distilled water, and fluoride was estimated in this solution by precipitation as lead chlorofluoride, using a volumetric determination of chloride in the precipitate by the Volhard method as described by VOGEL[12]. The standardization of this solution, $0.1417M$, did not appear to have altered after standing for several months in a glass bottle. 5 ml of the standard solution were diluted to 1 l; 1 ml of the diluted solution contained 13.46 μg fluorine.

Interferences

Recoveries of a known amount of fluoride were attempted in the presence of a few substances which might be expected to interfere with colour development. The types of interferences represented are:

1) increasing ionic strength, which causes bleaching;
2) competitive reaction with QAS, causing bleaching or intensification;
3) competitive reaction with fluoride causing intensification;
4) competitive reaction with aluminium, causing bleaching.

The recoveries obtained from flasks containing 27 μg fluoride and the stated quantities of other substances are given in Table I. These showed that for determinations where iron and aluminium were present in micro-amounts, and calcium, magnesium and phosphate were present in larger quantities, a preliminary separation of fluoride from these ions would be necessary.

TABLE I

RECOVERIES OF FLUORIDE IN THE PRESENCE OF OTHER SUBSTANCES

F taken = 27 μg

Substance	*Amount taken per 50 ml mmoles*	*μg F recovered*	*Substance*	*Amount taken per 50 ml mmoles*	*μg F recovered*
NH_4Cl	0.2	27.2	$MgSO_4$	5.0	27.2
	0.4	27.0		10.0	27.8
	0.8	27.8		20.0	27.8
	1.6	27.8		40.0	28.6
	3.0	27.4		100.0	29.6
$(NH_4)_2SO_4$	0.1	27.8	$CaCl_2$	5.0	27.2
	0.2	29.6		10.0	27.0
	0.4	31.8		20.0	26.2
	0.8	34.2		40.0	23.4
	1.6	37.4		100.0	16.6
$FeNH_4(SO_4)_2$	0.02	26.4	NaH_2PO_4	2.0	27.2
	0.04	24.8		4.0	27.0
	0.08	22.8		8.0	27.4
	0.20	16.4		16.0	27.8
				32.0	28.6
$AlK(SO_4)_2$	0.08	24.4			
	0.16	20.8	EDTA	0.5	46.6
	0.32	17.2		1.5	108
	0.80	2.2			

DETERMINATION OF FLUORINE IN ROCK-PHOSPHATE SAMPLE

An attempt was made to use the colour reagent for the determination of fluorine in rock phosphates. Since rock phosphates may contain appreciable quantities of iron and aluminium in addition to calcium, phosphate and fluoride, the interfering ions were removed by anion-exchange[13] before determining the fluoride.

Method

Samples of the rock phosphates were dissolved in alkaline ethylenediaminetetraacetic acid solution and aliquots containing 16–320 µg fluoride were added to columns packed with a strongly basic anion-exchange resin. The fluoride was eluted with 100 ml $0.025\,M$ ammonium chloride solution buffered at pH 9.2 with ammonia, leaving the interfering ions adsorbed on the column. 10-ml aliquots of the eluates were added to 50-ml graduated flasks, followed by 2 ml buffer and 10 ml colour reagent, and the solutions were made up to volume. The standards were prepared by adding 10 ml elutriant solution, 2 ml buffer and 10 ml colour reagent to 50-ml flasks containing 0, 10.8, 21.6, 32.4, 43.2 and 108 µg fluoride and making up to the marks. The absorbance of the solutions was measured at about 550 mµ using the solution containing 108 µg fluoride as a blank. A calibration curve was prepared from the readings of the standards and used for calculating the fluoride content of the solutions analysed.

Results

The determinations with different sample weights given in Table II show a tendency for the percentage of fluoride determined to decrease as the sample weight was increased. Further investigations showed that this was caused by the adsorption of some

TABLE II

ANALYSIS OF ROCK PHOSPHATES

Phosphate sample	*Wt. of sample taken* g	*Fluoride recovered* mg	% *F in sample*
Fluorapatite From Ontario	0.0802	2.73	3.40[a]
	0.1583	5.45	3.44[a]
	0.2513	8.61	3.43[a]
Rock phospate From Curaçao	0.0699	0.37	0.53
	0.1410	0.71	0.50
	0.2005	1.16	0.58
Rock phosphate From Tennessee[b]	0.0696	2.52	3.62[b]
	0.1411	4.98	3.53[b]
	0.2012	7.00	3.48[b]
Rock phosphate From Florida	0.0698	2.85	4.08
	0.1409	5.45	3.87
	0.1995	7.57	3.80
Rock phosphate From Morocco	0.0707	3.11	4.40[c]
	0.1400	5.87	4.19[c]
	0.2000	8.07	4.04[c]
Rock phosphate From Nauru	0.0686	2.15	3.14
	0.1385	4.32	3.12
	0.1996	6.02	3.02

Previous determinations by thorium nitrate titration[13]:

[a] 3.47, 3.44, and 3.48% fluorine.

[b] National Bureau of Standards, Standard Sample No. 56; 3.56, 3.47, 3.50, 3.56, 3.63 and 3.55% fluorine.

[c] 4.16, 4.26 and 4.12% fluorine.

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base from the elutriant solution during its passage through the anion-exchange column, which resulted in the pH of the test solution being slightly lower (0.01 – 0.04 pH unit) than the pH of the standards. The effect of this may be seen in Fig. 5, which shows the absorbance of the colour reagent over a range of pH from 3.4 – 5.4. A variation of ± 0.02 pH unit in the neighbourhood of pH 3.9 alters the absorbance by ± 0.008, corresponding with an error in the fluorine determination of about ± 1.1 μg fluoride per 50-ml flask. There was, therefore, a small additive error in the fluoride estimation, and a lower percentage error with the higher amounts of fluoride taken.

In order to reduce the difference in pH between the sample and standard solutions, a larger quantity of buffer was added to each flask, but the aluminium complex was then precipitated. In a second attempt to reduce the errors, both sample and standard solutions were neutralized before they were added to the colour reagent, but erratic results were obtained, probably because acetic acid has a low buffering action at pH 3.9.

The fundamental cause of the errors arises from using the colour reagent at pH 3.9. At pH 4.4, it is much less sentitive to pH changes but unfortunately also much less sensitive to fluoride, and so there is little prospect that the method can be made more accurate. However, the errors are not so large as to make the method unusable, and in the determination of fluorine in rock phosphate described here, the maximum variation was ± 0.18%, and the variation of the majority about ± 0.08%. In addition, there was tolerably good agreement with the values obtained by thorium nitrate titration, which are also given in Table II.

The method, which is simple to use, was found very suitable for the analysis of numerous samples provided that accuracy was not of first importance and was successfully used for the analysis of eluates from an anion-exchange column[13].

SUMMARY

A water-soluble sulphonate of quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) was prepared and its molar extinction from 220 – 600 mμ recorded. The reaction of this derivative with aluminium was investigated spectrophotometrically and it was found that a complex was formed which exhibited two absorption peaks, one at 265 mμ and one at 495 mμ. The latter absorption peak was used to examine the influence of fluoride ions on the complex, and at pH 3.9, the absorption was markedly decreased by fluoride. A procedure was developed to use this bleaching to determine small quantities of fluoride and it was applied to the estimation of fluoride in rock phosphates. This application showed, however, that the absorption of the reagent was dependent on pH to an extent which made the method accurate only when very close control of pH (± 0.01) was possible. However, its simplicity enabled the method to be applied to the semi-quantitative analysis of large numbers of solutions per day.

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Received April 8th, 1958

POTENTIOMETRIC TITRATION AT CONSTANT CURRENT OF COPPER(II) IN AMMONIACAL MEDIUM

by

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In recent years, several reviews[1-3] have been given of the relations between voltammetry and potentiometric titrations at constant current. While definitive experiments have been performed by several workers, no studies have been made in which the experimental titration curve could be compared with that calculated on the basis of voltammetry. The reason for this is that few couples are reversible at metal electrodes when a current passes through the system. In the present paper, it is shown that the copper(II)–(I) couple in ammoniacal medium yields current–potential curves which correspond to those for a reversible one-electron couple. The potentiometric titration at constant cathodic current of copper(II) with ethylenediaminetetraacetate has been studied, and the titration curve is shown to compare favorably with that calculated for a system in which one couple is reversible, and the reagent and reaction products are not reducible[4]. The titration of copper(II) with α-benzoin oxime, although approaching closely the calculated curve, is less accurate because the copper oxime precipitate interferes with the electrode reaction.

EXPERIMENTAL

C.P. chemicals and conductivity water were used to prepare all reagent solutions. Stock solutions of copper(II) sulfate were standardized electrogravimetrically. Standard solutions of ethylenediaminetetraacetic acid (H_4Y) were prepared as follows. The disodium salt was dissolved in water, and the free acid purified by twice precipitating it by the addition of perchloric acid. The dried acid was then dissolved in sufficient ammonium hydroxide (purified by isothermal distillation) to give a pH of 9.0 and diluted to volume; the principle species at this pH is HY^{-3}[5]. Amperometric titrations at −0.4 V *vs.* S.C.E. of the standard copper(II) solution with HY^{-3} in air-free pH 9 ammonia buffer established accurately the titer of the reagent (see Fig. 4a). An independent check upon the purity of the H_4Y was made by dissolving the acid in a minimum amount of tetramethylammonium hydroxide, complexing with a slight excess of the copper(II) solution, and titrating the liberated hydrogen ions with standard base[5]. The results of the two methods agreed within 0.2%; the purity of the recrystallized acid corresponded to 99.76%.

Platinum electrodes were prepared by sealing a short length of 18-gauge wire into the end of a 10-inch length of soft glass tubing. Electrical connection was made by filling the tube with mercury. The electrode was placed in a chuck and rotated with a synchronous motor about the axis of the tubing at 600 r.p.m. A Hume-Harris saturated calomel electrode was used for reference, and all potentials are referred to the S.C.E.

Current–potential curves were recorded automatically using a Sargent model XXI Polarograph with rates of change of potential of 0.074 and 0.148 V/min. A manual polarograph was used to maintain a constant current between the indicator and reference electrodes. Current measurements were made with a Weston model 430 microammeter (0–30 μA) with an internal resistance of 158.6

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ohms. No correction was made for the ohmic drop across the microammeter, and the current-potential curves are not corrected for residual currents. Potential measurements were made with a Leeds and Northrup Students potentiometer. All measurements were made at 25.0 ± 0.1°.

Reversibility of the copper(II)-(I) couple

Fig. 1 illustrates current-potential curves recorded from positive to negative potentials for the reduction of copper(II) in an ammoniacal buffer of pH 9.1 at a rotated platinum electrode with a sensitivity of 33 μA/mmole/l for the one-electron reduction of copper(II) to copper(I). The electrode sensitivity has been defined[6] as the magnitude of the limiting current observed for the given electrode reaction divided by the concentration of the electroactive species. The first of the two copper waves corresponds to the reversible reduction of $Cu(NH_3)_4^{+2}$ to $Cu(NH_3)_2^{+}$; the analysis of a typical wave is shown in Fig. 1 (i) in which $\Delta E/\Delta \log (i_1 - i)/i$ is calculated to be 0.064 V as compared with the theoretical value of 0.059 V. The half-wave potential of the first wave was observed to be —0.075 V *vs.* S.C.E. under these experimental conditions (Table I). The second of the waves corresponds to the incompletely reversible reduction to copper metal. Current-potential curves recorded from negative to positive potentials are more involved because the plated copper gives a dissolution pattern. After a curve

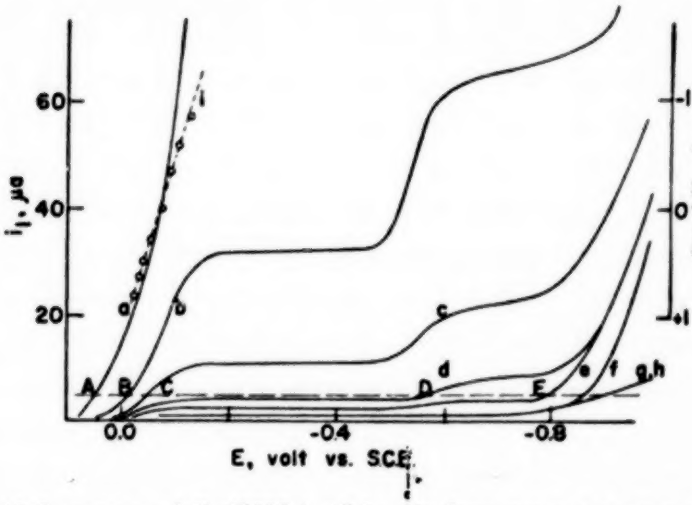

Fig. 1. Current-potential curves of $Cu(NH_3)_4^{+2}$ in air-free pH 9.1 ammonia buffer at rotated platinum electrode. $(NH_4Cl) = 0.1 M$, $(NH_4OH) = 0.02 M$, $k_{Cu^{+2}} = 33$ μA/mmole/l, (a) $(Cu^{+2}) = 1.10 \cdot 10^{-2} M$; (b) $1.01 \cdot 10^{-3} M$; (c) $2.99 \cdot 10^{-4} M$; (d) $1.00 \cdot 10^{-4} M$; (e) $5.00 \cdot 10^{-5} M$; (f) residual current; (g) $(CuY^{-2}) = 3.76 \cdot 10^{-5} M$; (h) $(HY^{-3}) = 4.00 \cdot 10^{-5} M$; (i) plot of $\log i/(i_1 - i)$ *vs.* E for data of curve b, slope = 1/0.064 V^{-1}.

TABLE I

HALF-WAVE POTENTIAL OF THE COPPER(II)-(I) COUPLE
AT ROTATED PLATINUM ELECTRODE IN pH 9 AMMONIA BUFFER
$(NH_4Cl) = 0.1 M$; $(NH_4OH) = 0.02 M$; $k_{Cu} = 33$ μA/mmole/l

(Cu⁺²), moles/l	*E½, V vs. S.C.E.*
$1.00 \cdot 10^{-4}$	-0.07_2
$2.99 \cdot 10^{-4}$	0.06_6
$1.01 \cdot 10^{-3}$	0.07_4
$3.09 \cdot 10^{-3}$	0.09_0
	average $-0.07_5 \pm 0.00_7$

had been recorded, the electrode was cleaned in nitric acid to remove the layer of copper before recording succeeding curves.

When copper(II) is titrated with ethylenediaminetetraacetate, the stable copper complex CuY^{-2} is formed. The electro-inactive behavior of the HY^{-3} reagent and of the CuY^{-2} complex is illustrated in curves g and h in Fig. 1. No evidence for the reduction of copper(II) from the complex is obtained as the hydrogen evolution starts before the copper is reduced.

Potentiometric titration at constant current using one indicator electrode

Consider the potentiometric titration at constant cathodic current of $+5\ \mu A$ of 0.01 *M* tetraamminocopper(II) with HY^{-3} at a rotated platinum electrode of previously stated sensitivity. Initially the potential of the electrode will be that on curve a in Fig. 1 at which the current is equal to $5\ \mu A$, $+0.05$ V at point A. When 91% of the copper(II) has been complexed and the tetraamminocopper(II) = 0.001 *M*, the potential will decrease to the corresponding point B on curve b, -0.01 V. If the current at which the titration is performed is small compared with the magnitude of the limiting current, the potential will decrease 59 mV per ten-fold decrease in the concentration of copper(II). When the concentration of copper(II) is reduced to a value sufficiently small such that the limiting current for the reduction of copper(II) plus the residual current is less than the titration current, the potential must shift to a much more negative value at which a current of $5\ \mu A$ can be maintained. In Fig. 1, the potential shifts from -0.05 V at C to -0.57 V at D and -0.75 V at E, and this sudden decrease in potential occurs very close to the equivalence point in the titration. In order for the jump in potential to practically coincide with the equivalence point, an electrode of much greater sensitivity than that in Fig. 1 is used in the actual titrations. The potential of the electrode beyond the end-point should remain constant at the potential at which the residual current is equal to the titration current, about -0.80 V in curve f.

The potentiometric titration at zero current of copper(II) in ammoniacal medium cannot be performed using a copper electrode because of the reaction between copper metal and copper(II) to form copper (I). At zero current, a platinum electrode does not respond to the activity of copper ions. However, at constant cathodic current, the concentration of copper(I) at the electrode surface is constant until very near the equivalence point, and the potential responds in the theoretical manner to a change in the concentration of copper(II).

Using the relations for a reversible system, and considering where necessary concentration over potential[4], the theoretical titration curve can be calculated. The potential of the electrode may be expressed[7] as

$$E = E_f^{\circ} + \frac{RT}{nF} \ln \left[C(1-y)\frac{v}{V} - i/k \right] \Big/ \frac{i}{k} \quad \ldots\ldots\ldots \quad (1)$$

where C is the initial concentration of copper(II), y is the fraction of the copper(II) which has been complexed, v is the initial volume and V the total volume of the solution, i is the titration current, and k is the sensitivity of the electrode for the reduction of copper(II) to copper(I). Fig. 2 compares an experimental titration curve with that calculated up to the potential break and also with that constructed from the current–potential curves shown in Fig. 1, assuming proportionality between electrode sensitivity and current. The experimental potential where 50% of the copper has been titrated is taken as the formal potential, Ef°, of the system, and the points on the theoretical curve are calculated from this potential. The theoretical and predicted curves agree well with that observed experimentally.

From equation (1) the potential of the platinum indicator electrode becomes indeterminate when the limiting current plus the residual current is less than the titration current, or when

$$y = 1 - \frac{iV}{kCv} \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

If, at this point, the potential of the electrode is determined by that of another couple which is appreciably different from the potential of the copper couple, a sudden change in potential is observed, and an end-point is obtained. Experimentally, it has been observed that an end-point determined by the maximum in the first derivative of potential with respect to concentration agrees well with the equivalence point. With the electrodes of large sensitivity (1700 μA/mmole/l) used in these titrations, the break in potential should occur 0.1% before the equivalence point. For six titrations of 0.00441 M copper(II) with 0.00901 M HY^{-3}, and average deviation of the end-point from the equivalence point of 0.08% was observed.

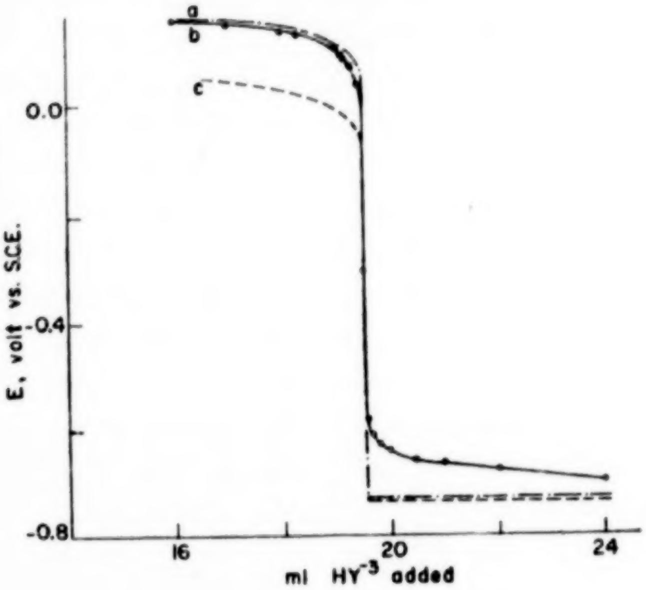

Fig. 2. Potentiometric titration at constant current = +5 μA of 0.00441 M $Cu(NH_3)_4^{+2}$ with 0.00901 M HY^{-3} in air-free pH 9 ammonia buffer with platinum electrode, $k_{Cu^{+2}}$ = 1700 μA/mmole/l: (a) theoretical, (b) experimental, (c) predicted from current–potential curves.

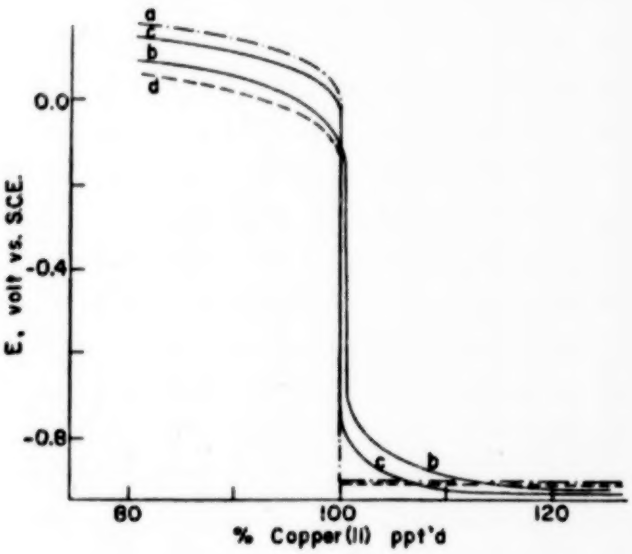

Fig. 3. Potentiometric titration at constant current = +2 μA of 0.00791 M $Cu(NH_3)_4^{+2}$ with 0.0643 M α-benzoin oxime in air-free pH 9 ammonia buffer, $k_{Cu^{+2}}$ = 120 μA/mmole/l: (a) theoretical, (b) experimental, without centrifuging, (c) experimental, with centrifuging, (d) predicted from current–potential curves.

Precipitation titrations using α-benzoin oxime

The potentiometric titration at constant current should be applied with care in systems in which a precipitate is formed during the titration. Precipitates often form films at the electrode surface and thus become a source of large resistance and, consequently, of interference. Curves a and b in Fig. 3 compare the theoretical and experimental curves for a potentiometric titration at constant current of +2 μA of 0.00791 M

copper(II) in air-free pH 9 ammonia buffer with a $0.0643M$ solution of α-benzoin oxime in 20% ethanol using a rotated platinum electrode with sensitivity of 120 μA/mmole/l. The experimental potentials are more positive than the theoretical values in the vicinity of the end-point, and 0.5 to 1.5% excess oxime is required to obtain the end-point. Only when the precipitate is removed from the solution by centrifugation (or filtration) after each addition of the oxime reagent and the potential measured with a clean electrode in a clear solution is an accurate end-point obtained (Fig. 3c).

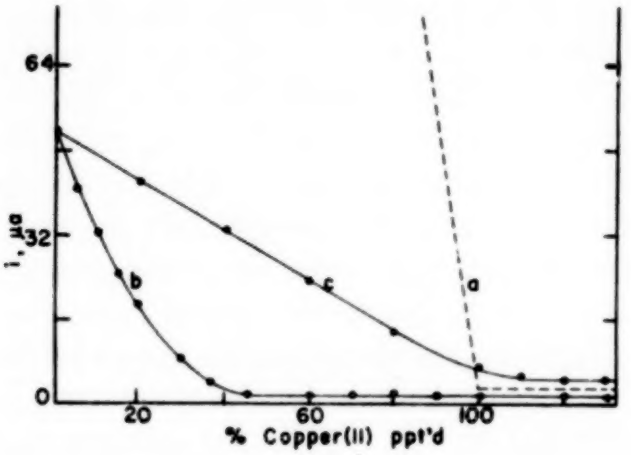

Fig. 4. Amperometric titration of $Cu(NH_3)_4^{+2}$ at $E = -0.4$ V in air-free pH 9 ammonia buffer a rotated platinum electrode: (a) titration of $0.00196M$ copper(II) with $0.00901M$ HY^{-3}, $k_{Cu^{+2}} = 1700$ μA/mmole/l; (b) titration of $0.00106M$ copper(II) using $0.0643M$ oxime, $k_{Cu^{+2}} = 48$ μA/mmole/l; (c) same as curve b, except precipitate removed by centrifuging after each addition of reagent.

An amperometric titration of copper(II) with oxime is also unsatisfactory under these conditions since, at constant potential, the limiting current is affected markedly by the presence of the precipitate at the electrode surface. Using HY^{-3} and oxime respectively, curves a and b in Fig. 4 compare the amperometric titration curves of $0.00106M$ copper(II) in air-free ammonia buffer at -0.4 V *vs.* S.C.E. In contrast with the well defined titration line using HY^{-3}, a linear relation between concentration and limiting current is not obtained using the oxime. If the precipitate is removed from the solution as done for the potentiometric titration, a straight titration line is obtained (Fig. 4c).

DISCUSSION

Most oxidation–reduction couples are incompletely reversible at solid electrodes, and their current–potential curves often depend greatly upon the pretreatment and characteristics of the electrode. It has been shown in another paper[8] that in such systems, the potentiometric titration curves can be predicted qualitatively, but not quantitatively, on the basis of the voltammetric behavior of the couple titrated and the reagent. As demonstrated in this paper, however, voltammetric titration curves can be predicted quantitatively if the redox couple is reversible at the electrode. The potentiometric titration at constant current of iodine with thiosulfate also gives a titration curve which corresponds to the calculated one since the iodine–iodide couple gives current–potential curves at a platinum electrode which correspond to those of a reversible system. The hexacyanoferrate(II)-(III) couple yields reversible current-potential curves at a rotated platinum electrode whereas the potentiometrically reversible (zero current) iron(II)-(III) couple does not[8]. The silver(I)-(0) couple is the only couple involving reduction to the free metal which has been reported to be voltammetrically reversible[7].

Systems containing precipitates may interfere with a titration even though the precipitate may be reduced with little or no overpotential. It has been demonstrated elsewhere[7] that layers of a silver halide on a silver electrode may exhibit sufficient resistance to interfere with both a potentiometric titration at constant current and with amperometric measurements. In this respect, the interference of the copper oxime precipitate in the titration of copper(II) deserves further investigation. While the presence of bulk precipitate at the electrode surface interferes with the diffusion layer and renders the amperometric titration in the presence of precipitate useless, this interference of the precipitate with the transport process obviously does not account for the failure of the potentiometric titration at constant current. If the precipitate behaved solely as a resistive film at the electrode surface, the experimental potentials should be more negative than the theoretical values, and the end-point should occur before the equivalence point. While the precipitate is electro-inactive under the conditions of classical voltammetry, it appears that a small quantity of the precipitate may be irreversibly reduced to form a tightly adherent film on the electrode; hence the potential of the electrode and the titration error are time-dependent functions of the titration current and the rate of addition of the reagent.

Potentiometric titrations at constant current retain some of the disadvantages of the titrations at zero-current; the time required for a titration at constant current is not appreciably shorter than that for the classical procedure. However, titrations at constant current may permit the determination of species under conditions which are not permitted in zero-current (*e.g.*, thermodynamic instability). Only one of the reactants need be electroactive, and the electrode reaction does not have to be rapid (reversible). The titration of very dilute solutions (0.001 M or less) is easily performed since the choice of anodic or cathodic titration currents facilitates attainment of a large potential break at the end-point.

SUMMARY

The voltammetric behavior of copper(II) in ammoniacal medium has been studied at a rotated platinum electrode. The copper(II)-(I) couple yields current-potential curves which correspond to those of a reversible one-electron reaction, but the reduction of copper(I) to copper(0) is incompletely reversible. The potentiometric titration at constant cathodic current of copper(II) with ethylenediaminetetraacetate compares well with that calculated theoretically. Similar titrations using α-benzoin oxime reagent are unsatisfactory because the presence of the copper oxime precipitate at the electrode surface interferes with the electrode reaction.

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Received March 28th, 1958

POTENTIOMETRIC TITRATIONS WITH AN ATTACKABLE ELECTRODE

THE BIMETALLIC ELECTRODE PAIR PLATINUM-TUNGSTEN

by

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INTRODUCTION

HOSTETTER AND ROBERTS[1] observed in 1919 that a palladium-wire electrode was not suitable as an indicator electrode for the potentiometric titration of iron(II) with dichromate using a depolarized electrode as a reference electrode, for no appreciable change in the potential was observed at the end-point. WILLARD AND FENWICK[2] and VAN NAME AND FENWICK[3] investigated extensively the use of two dissimilar metal electrodes in determining titration end-points, and observed two bimetallic pairs to be particularly useful for redox titrations: platinum *vs.* tungsten, and platinum *vs.* 10% rhodium-platinum alloy.

In a review of the relations between voltammetry and potentiometric and amperometric titrations[4], it was pointed out that the order of magnitude of the potential of an "attackable" electrode in a redox system can be predicted from the current-potential curves observed at such an electrode in an inert electrolyte on the one hand and the oxidation potential and poising capacity[5] of the redox system on the other. The notation "attackable" electrode is used in the classical sense and refers to a metal which is not noble and is oxidized in an inert electrolyte at potentials before oxygen evolution starts. Almost simultaneously with the publication of the above review, COURSIER[6] demonstrated that potentiometric titration curves using bimetallic electrode systems can be predicted from the current-potential curves of the individual electrodes. In the present paper the voltammetric behavior of a tungsten electrode in an inert electrolyte is given, and its use in a bimetallic electrode system is accounted for. The behavior of the rhodium-platinum alloy electrode will be discussed in a subsequent paper.

EXPERIMENTAL

C.P. chemicals and conductivity water were used to prepare all reagent solutions. Details have been described elsewhere[7].

Current-potential curves were recorded automatically using a Sargent model XXI Polarograph with rates of change of potential of 0.074 and 0.148 V/min. Current-potential curves are not corrected for residual currents. Potential measurements were made with a Leeds and Northrup Students Potentiometer. Potentials are referred to the saturated calomel electrode (S.C.E.). All measurements were made at 25.0 ± 0.1°.

Platinum and tungsten electrodes were prepared by sealing a short length (*ca.* 1/2 inch) of 24-gauge wire into the end of a 10-inch length of soft glass tubing. Electrical connection was made by filling the tube with mercury. The electrodes were rotated with a synchronous motor at 600 r.p.m.

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The electrode sensitivities[8] for the reduction of iron(III) in 0.1N hydrochloric acid were 120 and 360 μA/mmole/l at the platinum and tungsten electrodes respectively.

The residual current–potential curves at the tungsten electrode were observed to be irreproducible and largely dependent upon the treatment of the electrode prior to electrolysis. Current–potential curves, reproducible within 10% of the current magnitude, could be obtained after a suitable pretreatment of the electrode. A new electrode was immersed briefly in molten sodium nitrite to dissolve any oxide on the surface. The electrode then was washed with concentrated hydrochloric acid, followed by distilled water, and short-circuited with the S.C.E. in 0.1N perchloric acid. Starting from +0.1 V *vs.* S.C.E. to more positive potentials, fairly reproducible residual current–potential curves were now obtained which were independent of rates of change of potential less than ±0.2 V/min.

CHEMICAL AND ELECTRICAL CHARACTERISTICS OF THE TUNGSTEN ELECTRODE

The electrochemical behavior of the platinum and tungsten electrodes in an inert electrolyte solution were characterized by observing the residual current–potential curves in 0.1N perchloric acid. At the rotated platinum electrode, the residual currents were similar to those reported by KOLTHOFF AND TANAKA[9]. When the potential was scanned from negative to positive, a small anodic current corresponding to the formation of a platinum oxide film was observed prior to the oxygen evolution. The cathodic dissolution pattern of this film is observed when the potential is scanned from positive to negative.

A typical residual current–potential curve for the rotated tungsten electrode is shown in curve d in Fig. 1. The cathodic current corresponds to the evolution of hydrogen. The anodic current is indicative of the oxidation of the tungsten to a higher oxidation state, primarily to the tungsten(VI) oxide[10]. The electrochemical oxidation of tungsten is irreversible. Starting from very positive potentials (*ca.* 1.0 V) and scanning to more negative potentials, no evidence is observed for the reduction of the tungsten oxide. It is of interest to note that in 0.1N perchloric acid, the anodic wave corresponding to the evolution of oxygen at the rotated platinum electrode does not start until a potential of +1.2 V, while at the tungsten electrode, the anodic current for the oxidation of the metal to the tungsten oxide starts at about 0.0 V (attackable electrode).

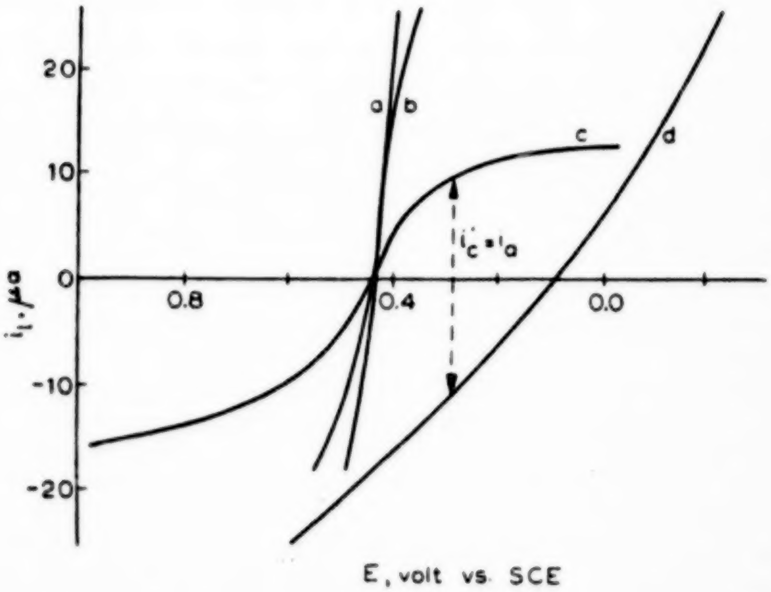

Fig. 1. Current–potential curves at rotated platinum electrode for equimolar solutions of iron(II) and (III) in 0.1N hydrochloric acid. (a) 0.01M iron(II) and (III), (b) 0.001M, (c) 0.0001M, (d) residual current at rotated tungsten electrode.

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Fig. 1 shows the current–potential curves for equimolar solutions of iron(II) and (III) of varying total iron concentrations in 0.1*N* hydrochloric acid at the rotated platinum electrode together with the residual current–potential curves at the rotated tungsten electrode. From these curves, one may estimate the zero-current potential that the tungsten electrode should exhibit in these solutions. This potential should be that at which the cathodic current for the reduction of iron(III), or any other oxidant, is equal to the anodic current for the oxidation of tungsten itself, *i.e.*, a mixed potential. For a qualitative intrepretation of the phenomena, we assume equal sensitivities for the platinum and tungsten electrodes and identical shapes for the iron(III) reduction curves at both electrodes. The dotted line in Fig. 1 predicts that the potential at which the anodic and cathodic currents in 0.0001 *M* iron solutions are equal would be +0.28 V at the tungsten electrodes as compared to +0.44 V at the platinum electrode. Current–potential curves for equimolar concentrations of iron(II) and (III) in 0.1*N* hydrochloric acid at the rotated tungsten electrode are shown in Fig. 2. In a similar manner, Figs. 3

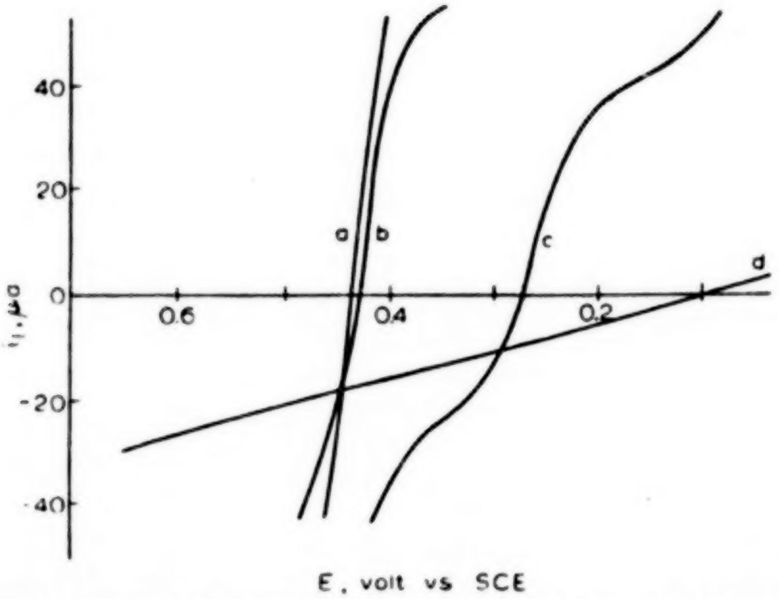

Fig. 2. Current–potential curves at rotated tungsten electrode for equimolar solutions of iron(II) and (III) in 0.1*N* hydrochloric acid. (a) 0.01 *M* iron(II) and (III), (b) 0.001 *M*, (c) 0.0001 *M*, (d) residual current curve.

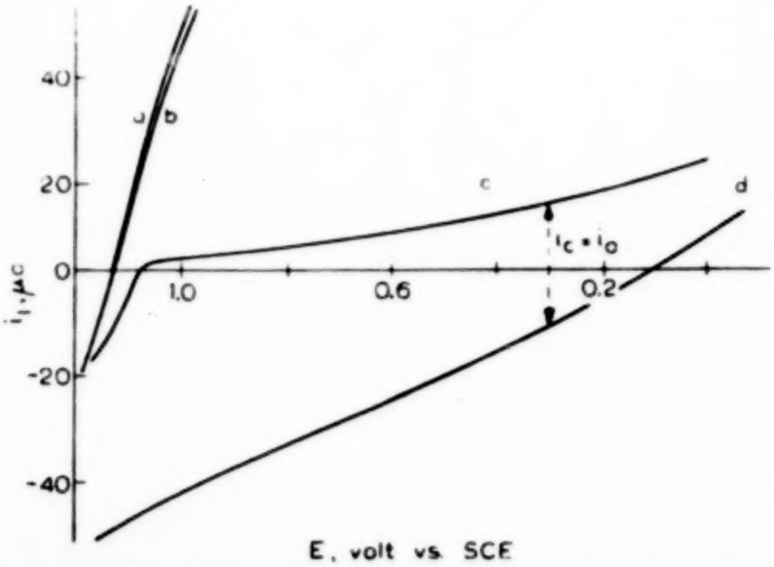

Fig. 3. Current–potential curves at rotated platinum electrode for equimolar solutions of cerium(III) and (IV) in 2*N* sulfuric acid. (a) 0.01 *M* cerium(III) and (IV), (b) 0.001 *M*, (c) 0.0001 *M*, (d) residual current at rotated tungsten electrode.

and 4 illustrate the current–potential curves for equimolar solutions of cerium(III) and (IV) of varying total cerium concentration in 1 *M* sulfuric acid at the rotated platinum and tungsten electrodes respectively.

Tungsten is not inert but is easily oxidized by iron(III) or cerium(IV). The rate of the chemical reaction between tungsten and iron(III) and cerium(IV) was measured semiquantitatively in order to ascertain whether the chemical reaction might play a

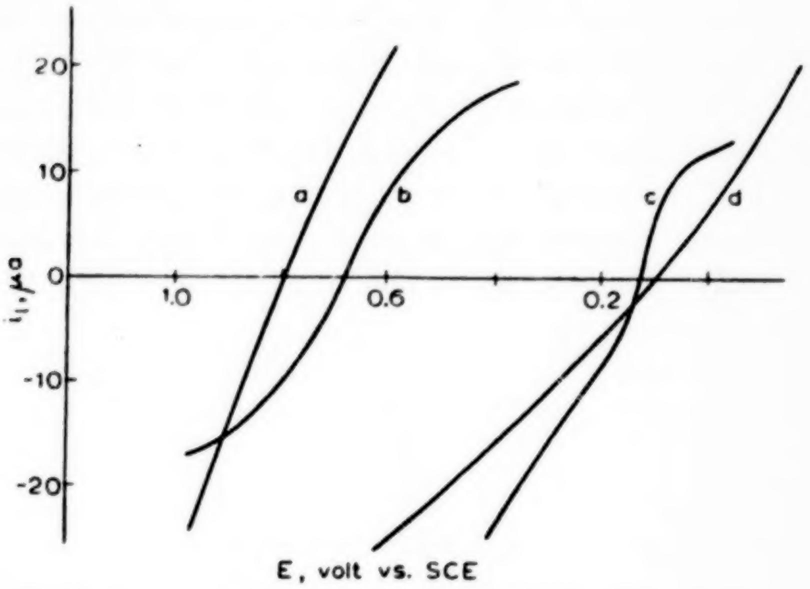

Fig. 4. Current–potential curves at rotated tungsten electrode for equimolar solutions of cerium(III) and (IV) in 2*N* sulfuric acid. (a) 0.01 *M* cerium(III) and (IV), (b) 0.001 *M*, (c) 0.0001 *M*, (d) residual current curve.

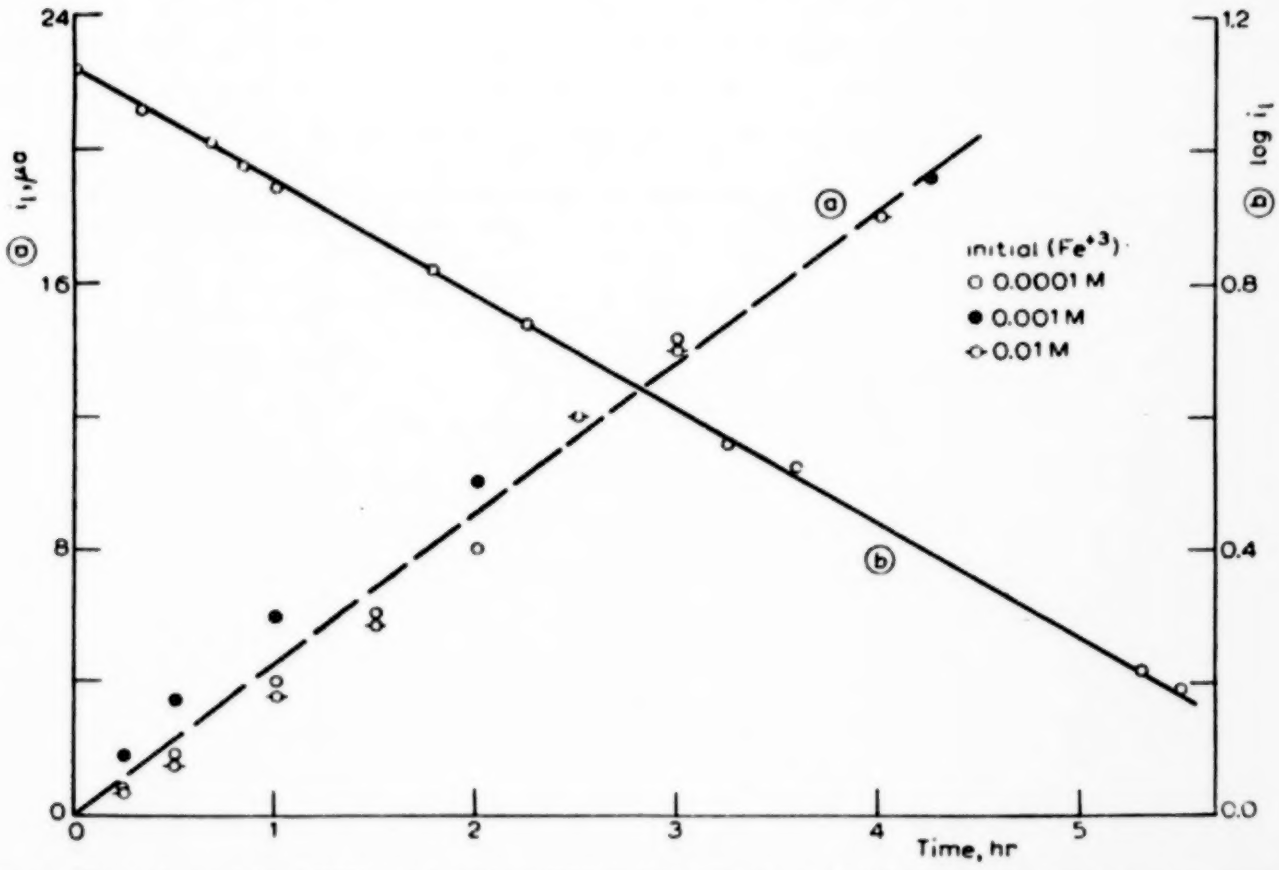

Fig. 5. Reaction of iron(III) and cerium(IV) with tungsten. (a) Increase in limiting current of iron(II) with time, $E = +0.60$ V, (b) decrease in logarithm of limiting current of cerium(IV) with time, $E = +0.50$ V, initial cerium(IV) = 0.0001 *M*.

significant role in establishing the tungsten potential in these systems. A 2-inch tungsten electrode was cleaned as described previously and then immersed in 50 ml of $2N$ sulfuric acid containing $0.0002M$ cerium(IV) or in $0.1N$ hydrochloric acid containing 0.01, 0.001, or $0.0001M$ iron(III). The solutions were stirred slowly at constant angular velocity, and the reaction was followed by measuring, at constant potential, either the increase in the limiting current of iron(II) or the decrease in the limiting current of cerium(IV) at a rotated platinum electrode. The change in the limiting currents with time for the various solutions is illustrated in Fig. 5. A zero-order reaction with respect to iron is indicated, the apparent rate of which is $2.0 \cdot 10^{-5}$ mole/l/h. After the reaction between tungsten and $0.01M$ iron(III) had proceeded for 72 h, the tungsten electrode was removed from the solution and examined. A finely divided, non-adherent black powder, presumeably tungsten(VI) oxide, was observed on the surface. The reaction between cerium(IV) and tungsten appears to be first order in cerium(IV) with a rate constant of 0.392 h^{-1}.

Tables I and II compare the zero-current potentials at platinum and rotated and stationary tungsten electrodes for varying concentrations of iron(II) and (III) and cerium(III) and (IV) solutions respectively. Comparison of the data in these tables with the curves in Figs. 1 to 4 allows the conclusion that, except in cerium solutions with low oxidation potential, the chemical reaction between tungsten and iron(III) or cerium(IV) has a minor effect in establishing the potential of the tungsten electrode

TABLE I

COMPARISON OF ZERO-CURRENT POTENTIALS AT ROTATED PLATINUM AND ROTATED AND STATIONARY TUNGSTEN ELECTRODES FOR VARYING CONCENTRATIONS OF IRON(II) AND (III) IN $0.1N$ HYDROCHLORIC ACID

Concentration (M)		*Measured e.m.f., V vs. S.C.E.*		
iron (III)	*iron (II)*	*Pt*	*rot. W*	*stat. W*
0.05	0.0005	+0.568	+0.56	+0.55
0.05	0.005	0.515	0.51	0.51
0.05	0.05	0.459	0.46	0.46
0.01	0.01	0.451	0.45	0.45
0.001	0.001	0.450	0.45	0.41
0.0001	0.0001	0.442	0.21	0.17
0.005	0.05	0.402	0.40	0.40
0.0005	0.05	0.345	0.34	0.33

TABLE II

COMPARISON OF ZERO-CURRENT POTENTIALS AT ROTATED PLATINUM AND ROTATED AND STATIONARY TUNGSTEN ELECTRODES FOR VARYING CONCENTRATIONS OF CERIUM(III) AND (IV) IN $2N$ SULFURIC ACID

Concentration (M)		*Measured e.m.f., V vs. S.C.E.*		
cerium (III)	*cerium (IV)*	*Pt*	*rot. W*	*stat. W*
0.044	0.00044	+1.254	+0.79	+0.79
0.044	0.0044	1.199	0.77	0.77
0.044	0.044	1.132	0.73	0.72
0.0088	0.0088	1.136	0.72	0.72
0.00088	0.00088	1.130	0.60	0.58
0.000088	0.000088	1.098	0.34	0.18
0.0044	0.044	1.075	0.66	0.63
0.00044	0.044	1.015	0.49	0.16

in the iron(II)-(III) or cerium(III)-(IV) systems. In 0.1*N* hydrochloric acid, the reduction waves for iron(III) solutions more concentrated than $10^{-3}M$ are very steep at the rotated tungsten electrode, and the zero-current potential is only slightly more negative than that at the platinum electrode (Fig. 2). In order to account for the large difference in the potential of the equimolar 0.0001*M* iron solution at the platinum (0.442 V) and at the rotated tungsten electrode (0.21 V), we must assume that in very dilute iron(III) solutions the iron(III) reduction wave has a much smaller slope than the slopes observed in the more concentrated solutions. The chemical reaction between iron(III) and tungsten cannot account for the large difference in potential, although the chemical reaction is responsible for the fact that the tungsten potential becomes more negative with time and is not well reproducible. In the very dilute iron solutions (0.0001*M*), the potential of the stationary tungsten electrode is more negative than that of the rotated electrode because iron(II) formed by the chemical reaction is present in much greater concentration at the stationary than at the rotated electrode. The electroreduction of cerium(IV) in 2*N* sulfuric acid is slow at the platinum electrode (see slope of curve c in Fig. 3). Apparently this rate is much smaller at the tungsten than at the platinum electrode (compare curves b in Figs. 3 and 4 respectively), thus accounting for the fact that the potential of relatively concentrated cerium(IV) solutions is considerably more negative at the tungsten than at the platinum electrode (Table II). For cerium solutions with low oxidation potential (E_{pt} less than [illegible] V in Table II), the tungsten potential is extremely irreproducible because the poising capacity[5] of the solution is low. For such systems, the role of the chemical reaction between cerium(IV) and tungsten in establishing the tungsten potential may become appreciable as may be shown by comparing the rate of chemical attack (Fig. 5) with the rate of electrochemical reduction (Fig. 4).

Thus we arrive at the conclusion that the potential of a redox system at an attackable electrode depends upon:

(1) the shape of the spontaneous anodic current-potential curve of the electrode in the supporting electrolyte;

(2) the concentration of the electroactive species and the degree of reversibility for the electrochemical reduction of the oxidized species. The smaller the concentration of the oxidized species and the smaller the degree of reversibility, the greater will be the difference between the true oxidation potential of the system and the potential measured at the attackable electrode;

(3) the true oxidation potential of the redox system. The more positive the oxidation potential, the greater will be the difference between the true potential and that of the attackable electrode, provided that the oxidized species in two systems is present at the same concentration and exhibits the same degree of reversibility;

(4) the rate of the chemical reaction between the attackable electrode and the oxidized species. As the rate of the chemical reaction increases, the current-potential curves will become more drawn out.

POTENTIOMETRIC TITRATIONS WITH TUNGSTEN AS THE REFERENCE ELECTRODE

The titration of 0.1*M* iron(II) with 0.1*M* cerium(IV) in 2*N* sulfuric acid was followed potentiometrically using the platinum-tungsten electrode pair. To simulate the composition of the solution before the equivalence point, increments of a solution of iron(II) sulfate in 2*N* sulfuric acid were added from an ultramicroburet to 50.0 ml of a solution containing 0.05M iron(III) sulfate and 0.05M cerium(III) sulfate in 2N sulfuric acid. The potentials of the platinum and rotated and stationary tungsten electrodes were measured against the S.C.E. Similarly the composition of the solution after the equivalence point was reproduced by adding increments of cerium(IV) sulfate solution to the above iron(III)–cerium(III) solution, and the potentials were measured. These potentials are plotted in Fig. 6, and the differences in potential between the platinum and tungsten electrodes are plotted in Fig. 7. Figs. 6 and 7 are of the same shape as those reported by WILLARD AND FENWICK[2] for the titration of iron(II) with dichromate or permanganate in acid solution. The shape of the curves in Fig. 7 corresponds qualitatively to that predicted from the data in Tables I and II. Before the end-point, the potential of the tungsten electrode is only slightly more negative than the true oxidation potential of the iron(II)–(III) couple. At and beyond the end-point, the potential of the tungsten electrode is much more negative than that of the platinum, which accounts for the fact that the tungsten electrode behaves as an internal reference electrode. Using the platinum–tungsten pair, the end-point determined by the first or second derivative of potential with concentration coincides within experimental error with that observed using the platinum–S.C.E. pair. However, the rate of the chemical reaction between the tungsten electrode and an oxidant, iron(III) or

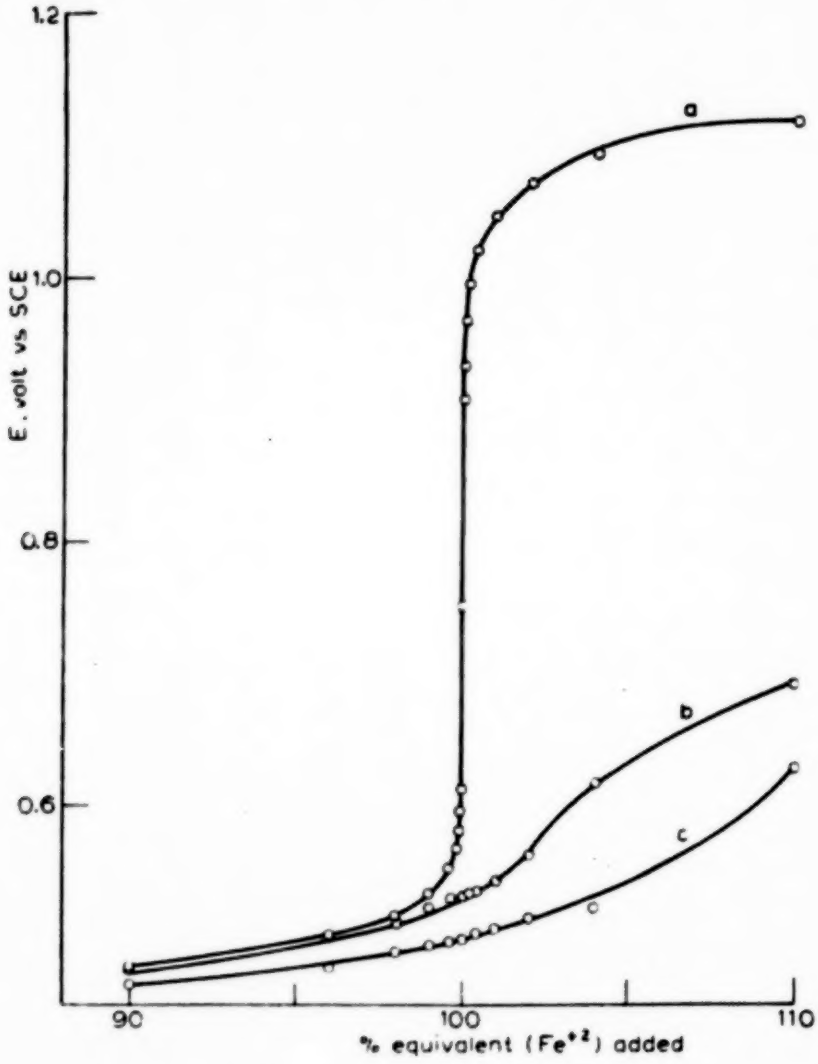

Fig. 6. Potentiometric titration of 0.1M iron(II) with 0.1M cerium(IV) in 2N sulfuric acid *vs.* S.C.E. (a) Platinum, (b) rotated tungsten, (c) stationary tungsten electrode.

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cerium(IV), is sufficiently great that the tungsten-platinum couple cannot be recommended for the titration of very dilute iron(II) solutions because of the reduction of iron(III) formed during the titration.

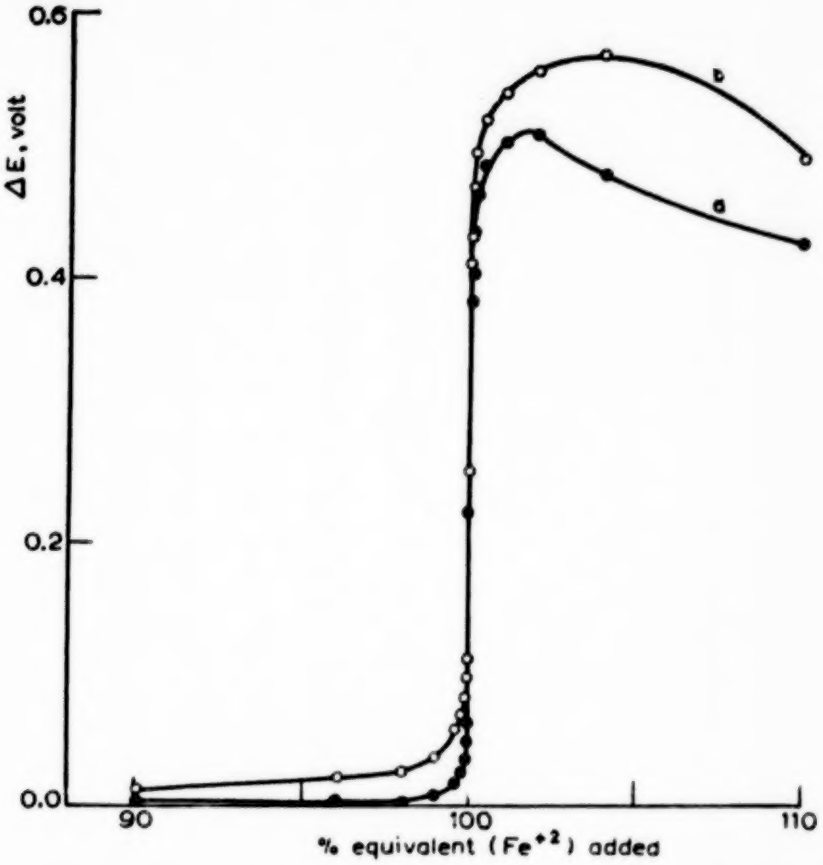

Fig. 7. Potentiometric titration as in Fig. 6. (a) Platinum *vs.* rotated tungsten, (b) platinum *vs.* stationary tungsten electrode.

SUMMARY

The potential of a redox system at a tungsten electrode is more negative than the true electrode potential when the electrode yields an anodic current in the supporting electrolyte alone at the oxidation potential of the system. The difference between the "mixed potential" at the tungsten electrode and the true electrode potential may be small or large. The various factors which determine this difference are discussed. The tungsten potential in iron(II)-(III) systems is fairly close to the true potential if the concentration of iron(III) is not too small. On the other hand, the tungsten potential in solutions containing cerium(IV) is always considerably more negative than the potential at the platinum electrode. This behavior accounts for the fact that the tungsten electrode serves as a reference electrode in the titration of 0.1 *M* iron(II) with 0.1 *M* cerium(IV).

Tungsten is attacked by oxidizing agents. The reaction was observed to be zero-order with respect to iron(III) and first order with regard to cerium(IV). The error caused by the chemical reaction is negligibly small in the titration of 0.1 *M* iron solutions with oxidizing agents but becomes significant in the titration of very dilute solutions.

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Received March 31st, 1958

POLAROGRAPHIC ESTIMATION OF SOLUBLE SILICA IN URANYL NITRATE

by

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Spectrophotometric methods[1] of analysis of soluble silica in uranyl nitrate are tedious and involve separations. A direct estimation would be convenient when moderate concentrations are involved. The present paper describes a direct method of estimating soluble silica in uranyl nitrate. This is based on combining the silica with ammonium molybdate in acid solution to form the silicomolybdate complex, which is then reduced at the dropping mercury electrode[2]. The current is proportional to the concentration of silica. Uranium does not interfere in the estimation and hence no separations are involved.

EXPERIMENTAL

Reagents

Silica solution. 500 mg of powdered quartz (E. Merck G.R.) was fused in a platinum crucible with 10 g of sodium carbonate (E. Merck G.R.) for one hour over a Mecker burner to a clear solution. The crucible was cooled and the contents extracted with cold water. The solution was made up to 500 ml and an aliquot was diluted to a suitable volume to give a standard solution of 100 γ of SiO_2 per ml.

Ammonium nitrate solution. 4*N* solution.

Ammonium molybdate solution. 12.5 g of ammonium molybdate (B.D.H.A.R.) dissolved in 250 ml of water.

Nitric acid. 9.2*N*.

Gelatin. 0.05%.

Apparatus

A "Du Bellay" polarograph was used for the experiments. Sensitivity was kept at $20 \cdot 10^{-3}$ μA per division. The mercury pool was used as the reference electrode and the temperature of the cell was maintained at 30 ± 0.5°. Oxygen was not removed in these experiments.

RESULTS

Estimation of silica

For the estimation of silica the following procedure was followed. 2.5 ml of ammonium nitrate 4*N*, 0.5 ml of ammonium molybdate stock solution, 0.2 ml of 9.2*N* nitric acid and 0.2 ml of gelatin 0.05% were pipetted into a 10-ml flask. The solution was then made up to 10 ml and shaken well for 5 min. The polarogram of the solution was taken from 0 to —0.15 V applied potential, using a mercury pool as anode without removing oxygen. Suitable aliquots of silica solution were then added to the above solution in different 10-ml flasks to give 10–100 γ of silica per 10 ml. Polarograms of these solutions were taken and it was found that —0.13 V was most suitable for reading the diffusion current. Fig. 1 gives a set of typical polarograms. The half wave potential was found to be +0.15 V *versus* S.C.E. Table I gives the values obtained for various amounts of silica after deducting the residual current values.

TABLE I

DIFFUSION CURRENT FOR SILICA AT —0.13 V APPLIED POTENTIAL

γ of SiO_2 added in 10 ml	*Total current in divisions*	*Diffusion current in divisions*	*Divisions per γ of SiO_2*
0	1.5	0	—
10	5.6	4.1	0.41
20	9.0	7.5	0.38
40	16.7	15.2	0.38
60	21.3	19.8	0.33
80	32.5	31.0	0.39
100	40.3	38.8	0.39

Mean divisions per $\gamma = 0.38$

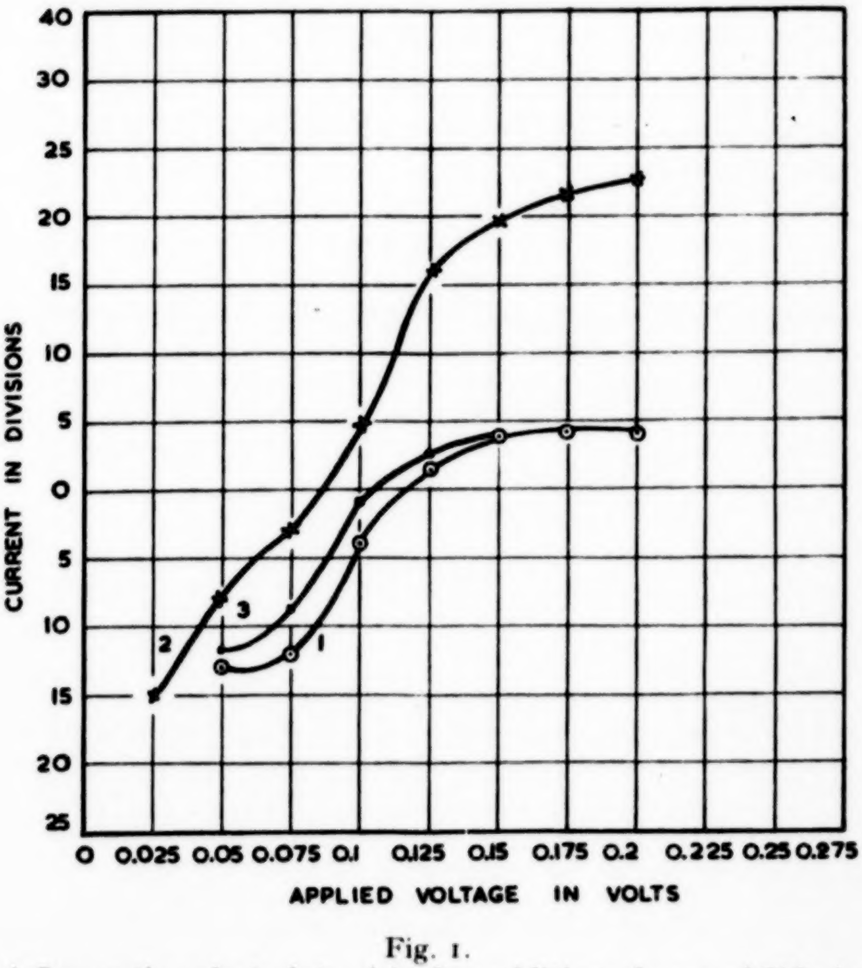

Fig. 1.

Polarogram of: (1) Supporting electrolyte; (2) after addition of 40 γ of SiO_2 in 10 ml; (3) after addition of 1 g of uranyl nitrate.

Estimation of silica in the presence of uranyl nitrate

The same procedure was followed. To the final solution of the supporting electrolyte 2 ml of uranyl nitrate solution containing 1 g of this substance were added. The solution was made up to 10 ml and the polarogram run. After deducting the residual current, the current at —0.13 V was taken as that resulting from the amount of silica in uranyl nitrate. This was verified by additions of further known amounts of silica to various uranyl nitrate solutions. The currents at −0.13 V corresponded to the silica added.

In Table II the results of the estimation of silica in uranyl nitrate are given. As little as 1 p.p.m. of silicon (2.14 p.p.m. of SiO_2) was determined in this way, the error being within ± 5% in the higher range and ± 10% in the lower ranges.

TABLE II

DIFFUSION CURRENT FOR SILICA IN URANYL NITRATE AT −0.13 V APPLIED POTENTIAL

Uranyl nitrate taken in g	*p.p.m. of SiO_2*	*Diffusion current in divisions*	*Error*
	10	3.6	−5%
	20	6.6	−12%
1	40	13.6	−10%
	60	24.0	+5%
	80	28.8	−5%
	100	38.0	0%
	2	4.0	+5%
5	10	18.8	−1%
	16	31.0	+2%

Interferences

Copper, iron and vanadium were found to interfere in this estimation. Ammonium citrate, oxalic acid and ethylenediaminetetraacetic acid (EDTA) were tried and found to be unsuccessful in removing these interferences. Copper interference was eliminated by the addition of 2 ml of saturated salicylic acid, while iron interference was also brought down to a minimum by this procedure. It was seen that iron could be tolerated to only 1 p.p.m. and vanadium to 5 p.p.m. Cadmium, thorium, cobalt, zinc, nickel, phosphorus and manganese in the order of 20–40 p.p.m. did not interfere. Chloride also does not interfere (0.1 mg).

ACKNOWLEDGEMENT

Thanks are due to Dr. V. T. ATHAVALE for his constructive criticism and helpful suggestions.

SUMMARY

A method is described for the estimation of soluble silica in uranyl nitrate based on the polarographic reduction of the silicomolybdate complex. Amounts as low as 2 p.p.m. of silica in uranyl nitrate can be estimated with an error less than 10%, no separations being involved. Vanadium and iron interfere and amounts above 5 and 1 p.p.m. respectively, cannot be tolerated.

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Received April 2nd, 1958

THE APPLICATION OF THIOSALTS IN ANALYSIS

II. ESTIMATIONS BASED ON THE DECOMPOSITION OF THIOSALTS

PART F. ESTIMATION OF SELENIUM AND TELLURIUM IN SELENITES AND TELLURITES

by

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The estimation of selenium or tellurium as sulphide, by the decomposition of the thiosalt formed with the alkali sulphide reagent, has already been proposed in an earlier publication[1]. Further investigations have shown that when selenium sulphide is precipitated by decomposing the thiosalt with $2N$ hydrochloric acid, the precipitated sulphide is highly gelatinous and difficult to filter. Moreover, it is not possible to dry the precipitated sulphide at 100–110° as it begins to soften at 100° and decomposes at a slightly higher temperature. Similarly, the precipitated tellurium sulphide is also unstable above 106°.

In this paper, it is proposed to give the exact conditions under which selenium and tellurium can be estimated as sulphide by decomposing the thiosalt.

EXPERIMENTAL

Estimation of selenium in a selenite

Measured volumes of standard solutions of potassium selenite[2] were treated with 50–60 ml of $2N$ sodium sulphide reagent[3] followed by enough $12N$ hydrochloric acid to give a final acidity of about $6N$. The mixture was heated nearly to boiling. During this operation the precipitated selenium sulphide changed its colour from yellow to orange. It was allowed to cool to room temperature, when selenium sulphide settled in the form of a crystalline precipitate which was very easy to filter. The precipitated sulphide was filtered through a weighed sintered glass crucible (porosity 4), washed thoroughly with distilled water, dried in an air-oven at 95° for 1 hour and weighed.

It was observed that 25–70 mg of the metal could be recovered with an accuracy of +0.06 to −0.2%.

Estimation of tellurium in a tellurite

It was observed that the thiosalt of tetravalent tellurium can be decomposed with $12N$ hydrochloric acid as in the estimation of selenium described above. It is not possible to dry the precipitate above 106°, as it is decomposed at a slightly higher temperature. As a precautionary measure the precipitate should never be dried above 105°.

Note: Estimation of tin as $SnS_2 \cdot 2H_2O$

When a solution containing tin is treated with $2N$ sodium sulphide reagent and the thiosalt decomposed by the addition of an excess of 2–$3N$ acetic acid, the precipitated sulphide has a marked tendency to peptize on washing with water. In order to overcome this difficulty it is essential to wash the precipitate with hot 2–$3N$ acetic acid followed by alcohol and ether successively before drying in vacuum and weighing.

SUMMARY

Modified procedures for the estimation of selenium, tellurium and tin when present in the tetravalent state, have been proposed.

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Received March 26th, 1958

THE APPLICATION OF THIOSALTS IN ANALYSIS

IV. A NEW SCHEME OF QUALITATIVE ANALYSIS

PART C

by

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In an earlier publication[1] a brief outline was given of a new scheme of qualitative analysis for the detection of basic radicals in mixtures containing only the common elements. Further investigations and experience have brought the following facts to light on account of which various modifications are proposed.

Table IV (see ref.[1]*)*

(a) In the precipitation of lead as sulphate and separation from other elements of the copper group, it is likely that bismuth oxysulphate, $(BiO)_2SO_4$, will also be precipitated owing to partial hydrolysis of bismuth sulphate.

It has been found that when the precipitate consisting of lead sulphate and bismuth oxysulphate is treated with a saturated solution of ammonium acetate, both the compounds go into solution. On adding acetic acid and potassium chromate, only lead is precipitated as lead chromate, leaving bismuth in solution. The latter can be precipitated as hydroxide by adding ammonium hydroxide and then confirmed by the sodium stannite test.

(b) When the filtrate, after the precipitation of bismuth as hydroxide, is treated with dilute hydrochloric acid and sodium thiosulphate, copper is precipitated as Cu_2S and not CuS. This precipitate may be dissolved in nitric acid (1:3) and tested for copper with potassium ferrocyanide.

(c) The separation of cadmium from cobalt and nickel with ammonium carbonate is not very sharp and is likely to involve complications when carried out by inexperienced operators. A better procedure is to treat the solution containing chlorides of cadmium, nickel and cobalt with ammonium hydroxide so that the acid is almost neutralized. The solution is further treated with sodium sulphide reagent acidified with dilute hydrochloric acid, whereby cadmium will be completely precipitated as yellow cadmium sulphide. The filtrate may be analysed for cobalt and nickel as usual.

Table V (*see ref.*[1])

It has been observed, that in the absence of iron, it is essential to eliminate phosphate by the basic acetate method, as it interferes with the analysis of the alkaline earths.

Table VI (*see ref.*[1])

The solution may contain Na_2CrO_4, Na_2ZnO_2, $NaAlO_2$ and phosphate (depending upon the presence of phosphate ions in the original mixture). On adding dilute nitric acid followed by ammonium hydroxide in excess, aluminium is precipitated as $Al(OH)_3$ and $AlPO_4$. Therefore, it is not possible to identify aluminium, in the presence of phosphate ions, by the cobalt nitrate test.

A modified procedure consists in treating the mixed precipitate with acetic acid, whereby aluminium hydroxide will go into solution leaving a residue of aluminium phosphate. The filtrate from aluminium phosphate may then be treated with ammonium hydroxide to precipitate aluminium as $Al(OH)_3$ and the latter confirmed by the cobalt nitrate test.

Alternatively the precipitate of aluminium phosphate and hydroxide may be dissolved in the minimum quantity of hydrochloric acid and aluminium confirmed with oxine solution.

Phosphate ions, however, do not interfere with the detection of zinc and chromium in the subsequent group analysis.

Table II (*see ref.*[1])

The precipitate may consist of SnS_2, Sb_2S_3 and very small amount of NiS. The latter does not interfere with the detection of antimony and tin.

SUMMARY

Several modifications for improving the efficiency of the new scheme of qualitative analysis have been proposed.

New procedures have been described for the detection of various metals of (a) the copper group (b) the iron and aluminium groups in the presence of phosphate ions.

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Received March 26th, 1958

REVUE DE LIVRE

Mises au point de chimie analytique pure et appliquée et d'analyse bromatologique, publiées sous la direction de J. A. Gautier, 6è Série, Masson et Cie., Paris, 1958, un volume broché de 172 pages et 60 figures, 2600 francs français.

Le sixième volume de cette collection dont j'ai déjà dit beaucoup de bien et souligné l'originalité et l'utilité comporte six conférences faites en 1957 à la Faculté de Pharmacie de Paris par MM.

P. Devillers – Analyse des produits sucrés industriels et commerciaux: échangeurs d'ions et chromatographie,

Cl. Duval – Applications analytiques de la thermogravimétrie,

J. A. Gautier – Chimie analytique et contrôle des médicaments,

H. Renault – Le dosage de radioéléments en biologie et en radiotoxicologie,

J. P. Wolff – Méthodes physico-chimiques d'analyse des corps gras, et se termine par un index récapitulatif des sujets traités dans les six premières séries de la collection.

Chaque article, accompagné de figures claires est suivi d'une abondante bibliographie et fait une mise au point moderne, scientifique qui permet à chacun de s'évader de sa propre spécialité. Ainsi pour s'en tenir à l'exposé de J. P. Wolff sur l'analyse des corps gras que l'on n'entrevoit habituellement que par la détermination d'un certain nombre d'indices traditionnels, nous trouvons ici les possibilités dans ce domaine de la chromatographie d'absorption et de partage, en phase vapeur, à contre-courant, la spectrophotométrie ultraviolette, dans le visible et dans l'infrarouge, la polarographie, le dosage potentiométrique, etc.

Clément Duval (Paris)

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